INSTITUTE OF METALS DIVISION

1939

A. I. M. E.

TRANSACTIONS

OF THE

American Institute of Mining and Metallurgical Engineers

and Petroleum

(INCORPORATED)

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Notice

This volume is the thirteenth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the Detroit Meeting, Oct. 17–19, 1938, and the New York Meeting, Feb. 13–16, 1939. The complete list of publications and proceedings, including the present volume, is as follows:

1908–1911 *Transactions* of the American Brass Founders' Association: 1908, Vols. 1 and 2; 1909, Vol. 3; 1910, Vol. 4; 1911, Vol. 5.

1912–1916 *Transactions* of the American Institute of Metals, Vols. 6–10.

1917–1918 *Journal* of the American Institute of Metals, Vols. 11–12.

1919–1926 TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.

1927–1928 PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, two volumes, of which the later is now designated Vol. 78 of the A. I. M. E. TRANSACTIONS.

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FOREWORD

The policy of publishing a separate volume of TRANSACTIONS for the Institute of Metals Division was inaugurated in 1927, and the nineteen technical papers in this thirteenth volume of the series are a valuable addition to the notable contributions to physical metallurgy which the members have made in previous years.

Our annual lecture was given by Professor Daniel Hanson, of the University of Birmingham, England, on "The Creep of Metals," and we are greatly indebted to him for his most interesting and instructive discussion of the problems connected with the correct evaluation of this particular physical property, which is of such great importance in many of the modern uses of metals. Professor Hanson's lecture is printed in this volume.

The membership of the Division is increasing and the work done by Dr. K. R. Van Horn, Chairman of the Membership Committee, and the other members is greatly appreciated.

Under the direction of Dr. D. K. Crampton, Chairman of the Papers and Programs Committee, and Dr. C. S. Smith, Vice-chairman, that committee has done work that deserves special commendation, not only in the selection of papers but in arranging programs, which are such an important part of the Division's activity.

As Chairman of the Division, I should like to express my deep appreciation of the generous and wholehearted assistance that has been given by the Chairmen and members of the Division Committees and Officers of the Division, and express my sincere thanks for their splendid cooperation.

ROBERT H. LEACH, *Chairman*,
Institute of Metals Division.

BRIDGEPORT, CONN.
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CONTENTS

Papers

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BYLAWS OF THE INSTITUTE OF METALS DIVISION

(As approved by the Board of Directors September 16, 1937; Art. VII, Sec. 7, approved March 17, 1939.)

ARTICLE I

Name and Object

Sec. 1. This Division shall be known as the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers.

Sec. 2. The object of the Division shall be to furnish a medium of cooperation between those interested in the metallurgy, fabrication and uses of the nonferrous metals and their alloys; to represent the A.I.M.E. in so far as nonferrous metallurgy is concerned, within the rights given in A.I.M.E. Bylaw XI., Sec. 1, and not inconsistent with the Constitution and Bylaws of the A.I.M.E.; to hold meetings for social intercourse and the discussion of nonferrous metallurgy; to stimulate the writing, presentation and discussion of papers of high quality on nonferrous metallurgy; to reject or accept such papers for presentation before meetings of the Division.

ARTICLE II

Members

Sec. 1. Any member of the A.I.M.E. of any class and in good standing may become a member of this Division upon registering in writing a desire to do so, but without additional dues.

Sec. 2. Any member not in good standing in the A.I.M.E. shall forfeit his privileges in the Division.

ARTICLE III

Funds

Sec. 1. The expenditure of the funds received by the Division shall be authorized by the Executive Committee of the Division.

ARTICLE IV

Meetings

Sec. 1. The Division shall meet at the same time and place as the Annual Meeting of the A.I.M.E., and at such other times and places as may be determined by the Executive Committee subject to the approval of the Board of Directors of the A.I.M.E.

Sec. 2. The annual business meeting shall be held within a few days before or after the annual business meeting of the A.I.M.E.

Sec. 3. At any meeting of the Division for which notice has been sent to the members of the Division through the regular mail at least one month in advance, a business meeting may be convened by order of the Executive Committee, and any routine business transacted not inconsistent with these Bylaws or with the Constitution or Bylaws of the A.I.M.E.

Sec. 4. For the transaction of business, the presence of a quorum of not less than 25 members of the Division shall be necessary.

ARTICLE V

Officers and Government

Sec. 1. The officers of the Division shall consist of a Chairman, two Vice-chairmen, Secretary and Treasurer. The office of Secretary and Treasurer may be combined in one person, if desired by the Executive Committee.

Sec. 2. The government of the affairs of the Division shall rest in an Executive Committee, in so far as is consistent with the Bylaws of the Division and the Constitution and Bylaws of the A.I.M.E.

Sec. 3. The Executive Committee shall consist of the Chairman, two Vice-chairmen, Past-chairman, Secretary, and nine members, all of whom shall be nominated and elected as provided hereafter in Article VII.

Sec. 4. The Chairman and Vice-chairmen shall serve for one year each, or until their successors are elected. Each member of the Executive Committee shall serve three years. The Chairman shall remain a voting member of the Executive Committee for one year after his term as Chairman.

Sec. 5. The Treasurer of the Division shall be invited to meet with the Executive Committee, but without ex-officio right to vote. He shall be appointed annually by the Executive Committee, from the membership of the Executive Committee or otherwise.

Sec. 6. The annual term of office for officers of the Division shall start at the close of the Annual Meeting of the Institute and shall terminate at the close of the next Annual Meeting.

ARTICLE VI

Committees

Sec. 1. There shall be six standing committees as follows: Papers and Programs Committee, Finance Committee, Data Sheet Committee, Membership Committee, Annual Lecture Committee and Annual Award Committee and such other Committees as the Executive Committee may authorize.

Sec. 2. It shall be the duty of the Papers and Programs Committee to secure the presentation of papers of appropriate character at meetings of the Division and of the A.I.M.E.

Sec. 3. It shall be the duty of the Finance Committee to inquire into and examine the financial condition of the Division and to consider proper means of increasing its revenue and limiting its expenses. The Finance Committee shall audit the accounts of the Division and report to the Executive Committee prior to the Annual Meeting of the Division. It shall render a budget to the Executive Committee estimating receipts and expenses for the ensuing year so that action can be taken on same at the first meeting following the Annual Meeting.

Sec. 4. It shall be the duty of the Membership Committee to encourage and solicit membership in the A.I.M.E. and in the Division in accordance with the Bylaws and Constitution of the A.I.M.E.

Sec. 5. It shall be the duty of the Annual Lecture Committee to arrange for the presentation at the time of the Annual Meeting of the A.I.M.E. of a lecture on a technical subject of particular interest to the Division and the A.I.M.E. as a whole. This lecture is to be known as the "Institute of Metals Lecture." This Committee shall make all arrangements, financial and otherwise, and render a complete report on same to the Executive Committee.

Sec. 6. The Chairman of the Division shall, subject to approval of the Executive Committee, appoint the Chairman and new members as required of the Committees referred to in Sec. 1.

Sec. 7. Appointments on standing committees shall be for terms of three years each with approximately one-third of the committee membership being appointed each year.

ARTICLE VII

Nominations and Elections of Officers and Committees

Sec. 1. Every year the Division shall elect a Chairman, two Vice-chairmen, a Secretary and three members of the Executive Committee.

Sec. 2. A Nominating Committee of five members of the Division shall be appointed by the Chairman of the Division subject to the approval of the Executive Committee.

Sec. 3. This Committee shall make its report to the Executive Committee not later than June 1.

Sec. 4. Any ten members of the Division may submit nominations for one or more offices to the Executive Committee not later than August 15, and the persons so nominated shall be included in the official ballot.

Sec. 5. The voting shall be by letter ballot.

Sec. 6. The ballots shall be counted by a committee of tellers appointed by the Executive Committee.

Sec. 7. The Executive Committee shall fill vacancies in any offices of the Division occurring for any reason other than the expiration of term of election.

ARTICLE VIII

Amendments

Sec. 1. Proposals to amend these Bylaws shall be made in writing to the Executive Committee and signed by at least ten members. They shall be considered by the Executive Committee and announced to the members through the columns of Mining and Metallurgy, together with any comments or amendments made by the Executive Committee thereon. They shall be voted upon at the annual meeting of the Division in February or by letter ballot, as may be directed by the Executive Committee.

ANNUAL AWARD CERTIFICATE OF THE INSTITUTE OF METALS DIVISION

In 1933, the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers established its annual award of an engraved certificate to the author or authors of the paper that in the opinion of the award committee represents the most notable contribution to metallurgical science among the papers that have been accepted by the Division for presentation at one of its meetings and have been published by the Institute within the three years preceding the date of award. The award is made by the Division each February.

There are no restrictions with respect to nationality, age or occupation of the author or authors.

Awards have been made as follows:

1934 Robert F. Mehl and Charles S. Barrett: Studies upon the Widmänstatten Structure, I—Introduction. The Aluminum-silver System and the Copper-silicon System. TRANSACTIONS (1931) **93,** 78–110.

1935 E. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda: The High-zinc Region of the Copper-zinc Phase Equilibrium Diagram. TRANSACTIONS (1934) **111,** 264–292.

1936 Cyril S. Smith and W. Earl Lindlief: A Micrographic Study of the Decomposition of the Beta Phase in the Copper-aluminum System. TRANSACTIONS (1933) **104,** 69–105.

1937 Arthur Phillips and R. M. Brick: Effect of Quenching Strains on Lattice Parameter and Hardness Values of High-purity Aluminum-copper Alloys. TRANSACTIONS (1934) **111,** 94–112.

1938 William L. Fink and Dana W. Smith: Age-hardening of Aluminum Alloys, I—Aluminum-copper Alloy. TRANSACTIONS (1936) **122,** 284–293.

1939 Frederick N. Rhines and Robert F. Mehl: Rates of Diffusion in the Alpha Solid Solutions of Copper. TRANSACTIONS (1938) **128,** 185–221.

THE INSTITUTE OF METALS LECTURE

An annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. In 1934 the Division established the custom of presenting a certificate to each lecturer.

A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
1923 Solid Solution. By Walter Rosenhain.
1924 The Trend in the Science of Metals. By Zay Jeffries.
1925 Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals. By Carl Benedicks.
1926 The Relation between Metallurgy and Atomic Structure. By Paul D. Foote.
1927 Growth of Metallic Crystals. By Cecil H. Desch.
1928 Twinning in Metals. By C. H. Mathewson.
1929 The Passivity of Metals, and Its Relation to Problems of Corrosion. By Ulick R. Evans.
1930 Hard Metal Carbides and Cemented Tungsten Carbide. By S. L. Hoyt.
1931 X-ray Determination of Alloy Equilibrium Diagrams. By Arne Westgren.
1932 The Age-hardening of Metals. By Paul D. Merica.
1933 Present-day Problems in Theoretical Metallurgy. By Georg Masing.
1934 Ferromagnetism in Metallic Crystals. By L. W. McKeehan.
1935 Gases in Metals. By C. A. Edwards.
1936 Diffusion in Solid Metals. By Robert F. Mehl.
1937 Refractories. By R. S. Hutton.
1938 The Nature of Metals as Shown by Their Properties under Pressure. By P. W. Bridgman.
1939 The Creep of Metals. By D. Hanson.

DANIEL HANSON

Institute of Metals Division Lecturer, 1939

The Creep of Metals

By Daniel Hanson*

(Institute of Metals Division Lecture†)

For most of their practical applications metals are required to withstand stresses of appreciable magnitude: indeed, it is because they possess the quality of resisting stress without becoming permanently deformed that they find such extensive use in the service of man. Metals and alloys must, in service, usually behave as elastic substances—or nearly so. It is not difficult to satisfy this condition at ordinary temperatures. Iron and its alloys, especially the steels, are at normal temperatures excellent elastic bodies, capable of satisfying most of the mechanical requirements of the engineer: where electrical, chemical or other properties are important, which cannot be met by steels, it is usually possible to find a nonferrous alloy such as nickel, copper or aluminum, which will prove satisfactory. When the metals or alloys are not inherently sufficiently elastic, cold-working or heat-treatment may develop elastic properties to a sufficient extent for practical needs. By means of relatively simple, rapid tests we can measure such properties as elastic modulus, limit of proportionality and proof stress, upon which design can be based with confidence.

The case of the soft metals, such as lead and tin, is well known to be exceptional. They possess no definite limit of elasticity, and the value of proof stress or tensile strength depends to a great extent on the speed with which the test is carried out. Design here must be based on other considerations than a well-established theory of the proportionality of stress and strain. It is now generally recognized that steels and nonferrous alloys possess at temperatures not greatly exceeding that of the atmosphere, characteristics quite different from those existing at ordinary temperatures, and that they assume qualities similar to those of the soft metals. Not only have they no limit of elasticity, but the proof stress and the ultimate stress depend on the time of application of the load. Flow under load may persist for long periods of time, possibly indefinitely, and the determination of a true maximum stress becomes a matter of great difficulty.

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* Professor of Metallurgy, University of Birmingham, England.

† Presented at the New York Meeting, February 1939. Eighteenth annual lecture. Manuscript received at the office of the Institute Feb. 9, 1939. Issued as T.P. 1071 in Metals Technology, June, 1939.

Although these facts had been known in a general way for many years, the full magnitude of the effects was certainly not realized until it was demonstrated quantitatively by the early work of Chevenard,[1] Dickenson[2] and French.[3] The work of Dickenson[2] in this respect was particularly valuable, for it was he who first carried out tests of long duration which demonstrated in a striking manner the serious weakness of even the strongest steels when held at high temperatures for prolonged periods. The publication of Dickenson's work did much to focus attention on this important subject: in particular, it showed the inadequacy of the short-time tensile test as a guide to high-temperature strength.

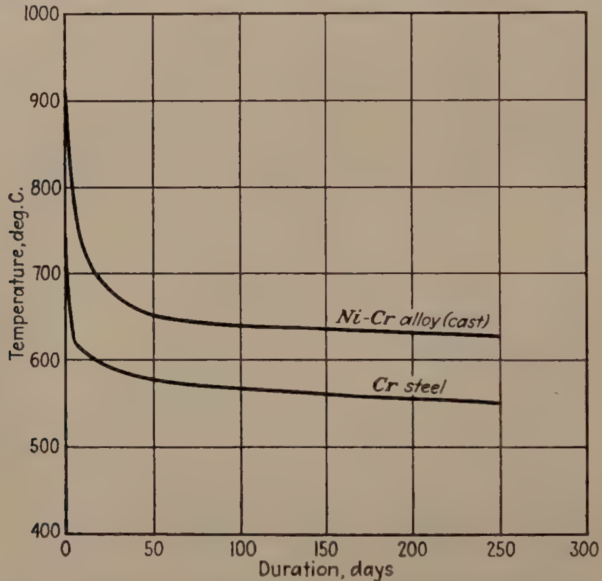


Fig. 1.—Temperature-duration curves (Dickenson).

In Dickenson's tests, the load was maintained at the constant value of 8.5 tons per sq. in. and the time to fracture under this load was measured at various temperatures. His results were plotted in the form of temperature-duration diagrams, of which two examples are shown in Fig. 1. The form of these diagrams suggested that there might be a temperature below which the applied load of 8.5 tons per sq. in. would not cause fracture, even if applied indefinitely; Dickenson himself claimed that a linear law existed between the temperature and the logarithm of the time to fracture, thus implying that failure would take place at any temperature after a sufficient time, but this conclusion was, in fact, hardly justified, his tests being, as we know now, too crude to give more than a general indication of the behavior of the metals.

[1] References are at the end of the paper.

Many workers have plotted the applied load against the duration, temperature being held constant; similar curves were obtained, some examples being given in Fig. 2. These raised the question as to whether there exists at a high temperature a stress which is insufficient to break the material no matter how long it is applied. This conception of a "limiting creep stress," under which the metal will never break, was very attractive to metallurgists and engineers because it appeared to offer the soundest possible basis for design at high temperatures. Much attention, therefore, has been devoted to a study of the exact shape of this stress-duration curve. The desirability of such study was quite clear, for there was ample practical experience of metals in service at elevated temperature to show that in many instances very useful service stresses could be sustained during a service life of many years without any sign of imminent failure. In view of this experience it was difficult

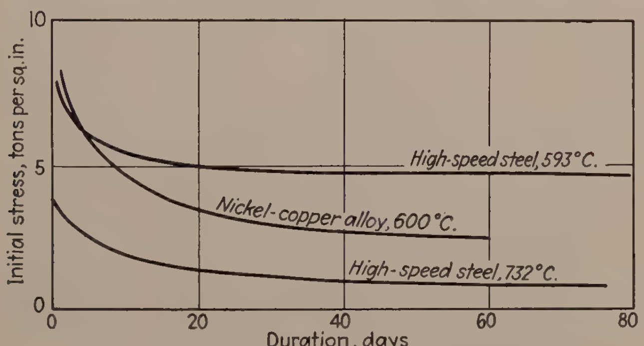


FIG. 2.—STRESS-DURATION CURVES (TAPSELL).

to accept the conclusion that metals must ultimately break under any stress at high temperature, however small, when most of the evidence was based on tests of only a few weeks duration.

STRESS-DURATION CURVE

The form of the curves in Fig. 2, which are quite typical, show that the duration increases much more rapidly than the stress decreases. The curves suggest that the relationship might be expressed in a hyperbolic form, with asymptotes at positive values of stress; or in an exponential form indicating ultimate failure at all stresses but with very long duration when the stresses are low. A satisfactory examination of this question is rendered difficult by the fact that comparatively few tests have been carried out at a duration of more than a few months; a critical answer therefore is somewhat difficult to obtain.

The validity of an exponential relationship can be checked by plotting the stress against the logarithm of the duration. Such curves become straight lines if the exponential law is true. Fig. 3 shows such a plotting

for a mild steel at 293° C. and 432° C. (French), a nickel-copper alloy at 500° C. and 600° C. (N.P.L.) and two tin alloys at 20° C. (Hanson and Sandford). It is quite clear that in these instances the exponential relationship does not hold; sometimes tests of comparatively short duration appear to conform to this relationship, as is indicated in some of the curves, but tests of long duration usually give curves that are far from straight lines. The existence of a definite limiting creep stress would be indicated if the curves became asymptotic to some positive value of

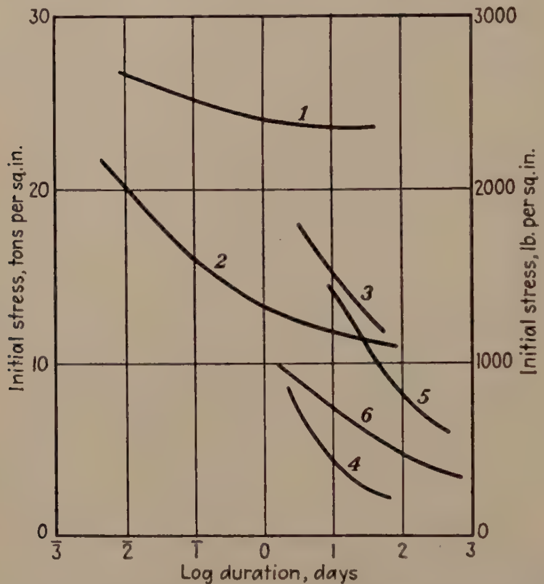


FIG. 3.—STRESS-DURATION CURVES, SEMILOG PLOT.

1. 0.24 per cent C steel, 293° C. (French)
2. 0.24 per cent C steel, 432° C. (French)
3. Nickel-copper alloy, 500° C. (N.P.L.)
4. Nickel-copper alloy, 600° C. (N.P.L.)

} Left-hand scale.

5. Tin containing 1 per cent Bi (Hanson and Sandford)
6. Tin containing 0.04 per cent Ag (Hanson and Sandford)

} Right-hand scale.

stress, but there is no indication of this, in these or any other reliable curves, and it is quite impossible to indicate from the shapes of the curves their probable form for very long durations; they are, on the contrary, quite consistent with the persistence of creep over very long periods of time.

A hyperbolic relationship also appears to apply in some instances for low durations, but the curves so obtained appear to indicate a limiting stress for infinite duration greater than seems consistent with the results of other tests, such as those in which the stress for very long life is estimated from the rate of creep over a shorter period. A final decision on this point must await the carrying out of extremely lengthy tests under

rigid conditions of control; the number of such tests at present available is insufficient to allow any final conclusion to be reached.

Another method of representing the results of stress-duration curves consists in plotting the logarithm of the stress against the logarithm of the duration, a method that is very useful when both the variables have values extending over a wide range. With such a plotting, a power relationship such as $D^n = bS^n$ gives a straight line. Fig. 4 shows the same results as are given in Fig. 3, but with log-log plotting. All the curves are convex downwards, and it is impossible to predict their shapes for long durations.

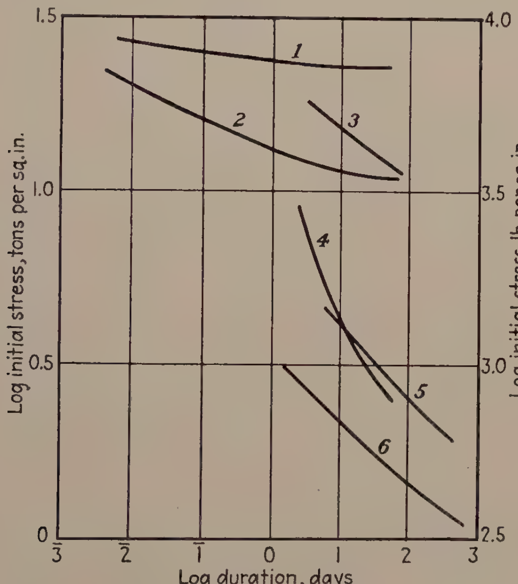


FIG. 4.—STRESS-DURATION CURVES, LOG-LOG PLOT.

To prove the existence of a true limiting creep stress for infinite endurance is clearly a matter of difficulty by the methods I have outlined. All variations in temperature, during one test or between different tests, of the order of 5° C. or less, introduce errors in duration sufficient to make reliable tests impossible, while temperature gradients along the specimens, or even small variations in properties of duplicate specimens cut from the same bar, introduce errors of appreciable magnitude from the present point of view. Only by the most carefully controlled tests of long duration can we hope to determine the law connecting load and life.

CREEP STRAIN

We have so far considered the problem only in relation to stress, duration and temperature, without reference to the strain which may

take place during life. Design is, however, usually as much concerned with strain as with stress, for the amount of deformation that can be tolerated during the life of a metal at high temperatures is clearly limited, and the number of applications in which extensions of as much as 1 per

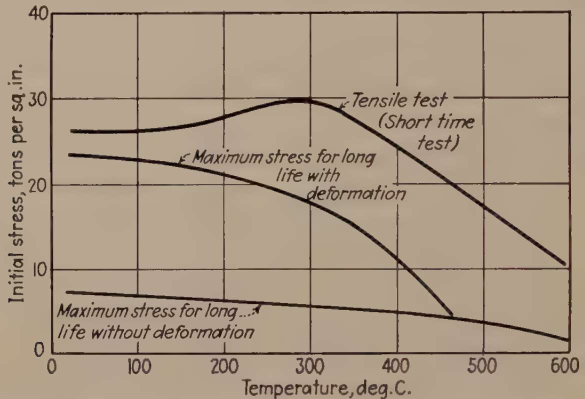


FIG. 5.—SHORT AND LONG TIME TESTS FOR 0.24 PER CENT C STEEL (FRENCH).

cent during life are tolerable is very limited. Moreover, the permissible tolerances for different types of service vary very greatly, being very small in some instances, such as turbine cylinders and the like, but quite substantial in other applications.

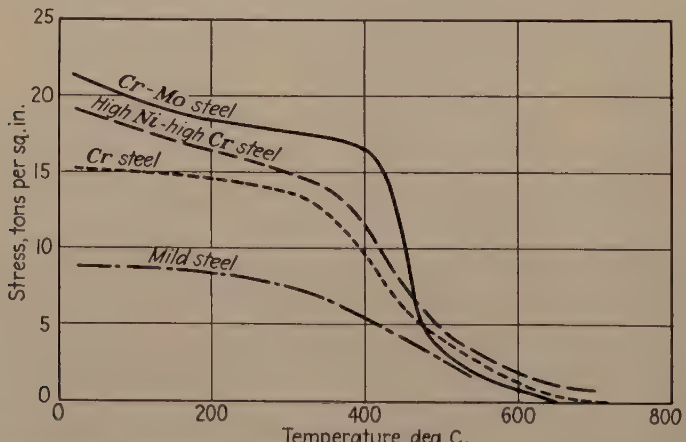


FIG. 6.—STRESS TO PRODUCE 0.1 PER CENT DEFORMATION IN 1000 HOURS (FRENCH, CROSS AND PETERSON).

It is now quite well recognized that, even at stresses which can be withstood for long periods, perhaps indefinitely, creep of intolerable amounts may occur. Engineers are therefore faced with the alternatives, either that design stresses must be reduced to extremely small magnitude by the use of large sections, which are often inconvenient, or that small

amounts of creep must be accepted. French[4] was probably the first to draw serious attention to this aspect of the question, and in Fig. 5 is reproduced a diagram which he published in 1926 showing the results of long-time tests on a 0.24 per cent carbon steel. For temperatures below about 460° C. he clearly distinguishes between maximum stress for long life with deformation and maximum stress for long life without deformation. Although these results refer to tests in which the times to cause fracture did not in any case exceed 24 days, and the actual values given would probably now be regarded as quite unacceptable, his work drew attention to a very important consideration in creep testing. A year later, French, Cross and Peterson[5] expressed the opinion that creep-test results could be better represented by a series of curves setting out the stress-temperature relationship for each material based on a definite amount of creep during a predetermined time. Fig. 6 shows the variation with temperature in the stress required to produce 0.1 per cent deformation in 1000 hr. While the methods used by these investigators lack the refinement customary in creep testing today, their work was fundamentally important in that it drew attention to the importance of elongation, and indicated the lines on which it could best be dealt with in creep testing. Now that the view is generally accepted among engineers that at elevated temperatures flow occurs to some degree at any practical stress, the accurate measurement of strain has become all important.

Strain-time Curve at Constant Load

The phenomena associated with flow are best represented by strain-time curves at constant load. Such curves are not only practically important as giving the basis from which working stresses may be estimated, but they also deserve attention as having a bearing on the theory of creep. In general, the curve representing the behavior with time of a specimen to which a constant load is applied may be divided into four parts, which are represented in Fig. 7. Since nearly all creep testing is carried out in tension we will consider the effect of a tensile load. The first application of the load produces an immediate elastic extension, which may be accompanied by a certain amount of plastic flow; during the second stage the extension continues, but at a decreasing rate, until a minimum rate of creep is obtained at which the third stage may be said to begin; during the third stage the creep rate remains constant, and this is succeeded by the fourth stage, during which the rate of creep accelerates until fracture occurs. This form of curve is best developed in tests carried to the point of fracture at moderate temperatures; under other conditions one or more of the stages may be absent or undetectable. For example, tests carried out at comparatively high temperatures may exhibit an accelerating rate throughout, while tests at comparatively low temperatures under low stresses may produce curves in which the creep

rate declines continuously during the period of the test and indeed may become immeasurably small. Curves of these types are shown in Fig. 8. In most instances, the total extension at the point at which the final stage

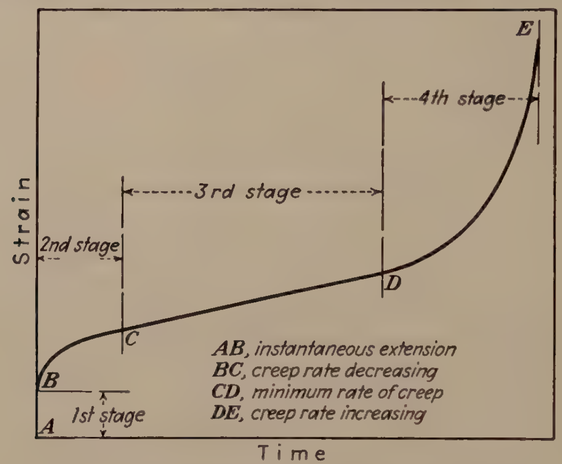


FIG. 7.—GENERAL FORM OF STRAIN-TIME CURVE.

begins is excessive for all practical purposes, and usually the conditions of stress and temperature are so selected that this stage is not entered.

There has been much speculation in metallurgical literature as to the cause or causes of the form of this creep curve. The simplest and most

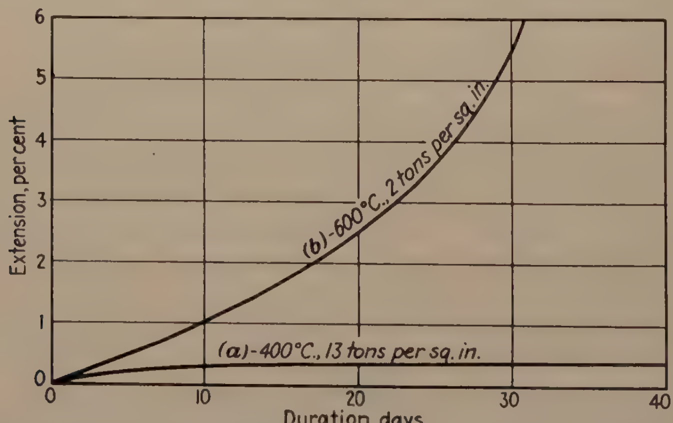


FIG. 8.—DECLINING (a) AND ACCELERATING (b) RATES OF CREEP. TESTS ON 0.44 PER CENT C STEEL (TAPSELL).

obvious explanation is to regard the whole curve as a running balance between the effect of work-hardening on the one hand and recrystallization or annealing on the other. According to this explanation the period of declining creep rate is characterized by the predominance of the cold-

working effect over the recrystallization effect, but to a declining extent as the total strain increases; the period of constant minimum creep rate is held to be due to an exact balance between the cold-working and annealing effect; while the third stage is initiated by stress intensification due to the diminishing cross section and necking of the specimen. There is, of course, plenty of evidence that these factors play an important part in determining the behavior of metal under stress at high temperatures, but there are features of creep, revealed both by metallographic and by mechanical methods of investigation, which reveal a more complex mechanism of flow.

From the practical point of view, the exact shape of the strain-time curve is very important. In most forms of creep testing now in use the permissible stress has to be estimated from strain-time curves with

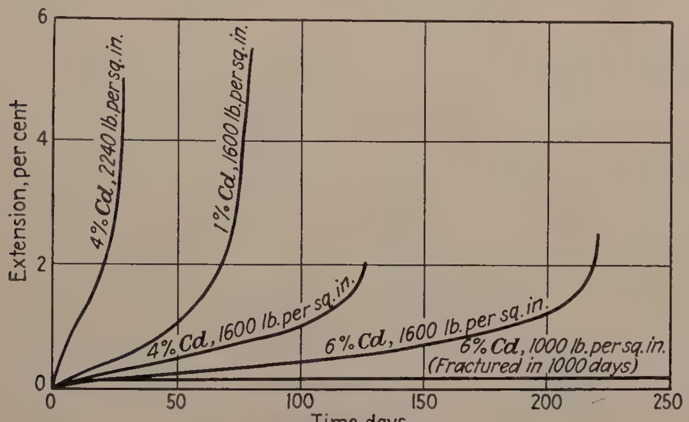


FIG. 9.—CADMIUM-TIN ALLOYS QUENCHED FROM 170° C. AND TEMPERED AT 120° C.

reference to the maximum permissible deformation in service. If tests of short duration are to be possible, it is clearly necessary to know exactly the form of the strain-time curve in order to make reliable extrapolation. The most important part of this curve from this point of view is that representing the declining creep rate, for this is the region within which designers naturally prefer to work if possible. The constant rate of creep, which is also the minimum rate for the particular stress and temperature involved, is also important, for it represents a definite characteristic of the material under the conditions pertaining to the test. For a given temperature it is a factor only of the stress and for a given stress a factor only of the temperature, and it is therefore an important factor in determining the creep characteristics of a material. In Fig. 9 is shown a series of creep curves of tin at various stresses. Each curve exhibits a period of decreasing creep rate, and the following additional points may be noted:

1. The minimum rate of creep occurs after a longer and longer period as the stress is decreased.

2. The minimum rate is maintained for a longer period of time the lower the stress.

With lower stresses or temperatures, the minimum rate of creep may never be attained, and with higher stresses or temperatures, the minimum rate may always be exceeded.

Various attempts have been made to evaluate the declining creep rate mathematically. McVetty[6] has attempted a solution on the basis that the constant creep rate is approached asymptotically, and he shows that an exponential function with appropriate constant represents actual creep curves closely. Kanter,[7] dealing with the creep of steel at 400° to 540° C. found continuously decreasing creep extending over a period of a year or longer, suggesting complete cessation of creep eventually. Some of these data gave linear curves when plotted with strain and time ordinates both logarithmic and may be represented by an equation in which creep strain is a power function of time. Tapsall and Prosser[8] plotted the results of lengthy creep tests using a linear strain ordinate and a logarithmic time ordinate. Their results fitted closely onto straight lines, indicating that the rate of creep in their experiments was inversely proportional to the time of constant stress application. Further elucidation of these relationships is required, because creep tests as now carried out commonly involve declining rates of strain. The estimation of working stresses involves the prediction of behavior for times very greatly exceeding those of the creep tests themselves, and the establishment of a reasonable strain-time relationship would remove some serious difficulties at present associated with creep testing.

Constant Creep Rate

The minimum rate of creep sometimes occurs only at a point of inflection, and this is especially true in creep at high temperatures or under high stresses. Some such curves are shown in Fig. 9, those corresponding to the higher stresses having only a point of inflection. In such instances, the form of the curve in the region of the point of inflection is clearly determined by the balance between the factors making for a declining rate and those favoring an increasing rate of strain. Such instances are not, however, practically important; usually the engineer is more interested in conditions that favor creep at constant or nearly constant rates for long periods.

The fact that in some instances the minimum creep rate appears to be maintained for substantial times suggests that the flow during this period may be in the nature of viscous flow. This implies that the metal should behave homogeneously and that the density and other characteristics should be unaffected by the strain. There is nothing

fundamentally impossible about this conception, though its experimental establishment might be a matter of difficulty with slow rates and low total amounts of creep owing to the smallness of the internal changes. Bailey[9] has put forward the view that continuous creep is possible because the strain-hardening produced by flow is automatically compensated by softening at the temperature of the test. Clark and White[10,11] and Jenkins[12] refer to the period of minimum creep rate as being characterized by continuous recrystallization of the strained material. The latter theory certainly appears to indicate the possibility of something very like true viscous flow, but there are difficulties in this explanation with which I propose to deal later.

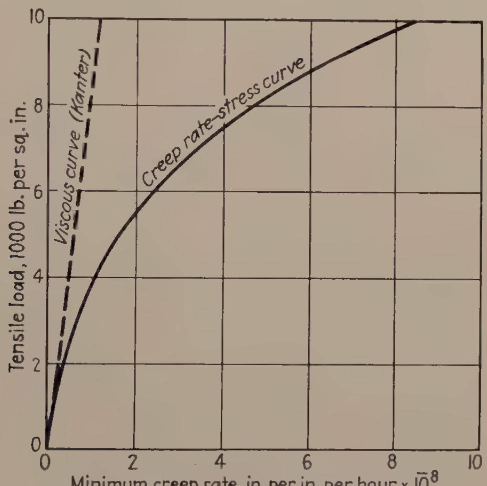


FIG. 10.—CREEP RATE-STRESS CURVE.

True viscous flow is expressed by the equation

$$V = kS$$

where V is the velocity of flow and S is the strain. The form of the curve connecting creep rate with tensile load, for very small stresses, is given in Fig. 10 (Kanter[7]). This indicates a very rapid increase in the creep rate as the stress increases, and it is clear that truly viscous extension does not occur over any wide range of stress. The curve does, however, indicate the possibility that at very low rates of strain truly viscous phenomena may be involved, and definite evidence that this is sometimes true is now forthcoming in a number of directions; Chalmers[13] has shown that at low rates of elongation the flow of single crystals of tin is viscous, but that above a certain rate it becomes plastic. His results are shown in Fig. 11.

Similar results have been obtained by Hanffstengel and Hanemann[14] and by Moore and Beckie[15] for the flow of lead under low stresses. Both

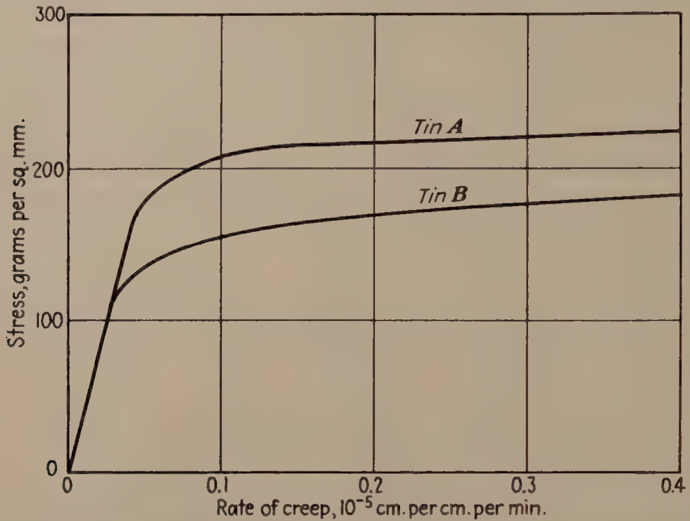


FIG. 11.—CREEP RATE-STRESS CURVE FOR SINGLE CRYSTALS OF TIN (CHALMERS).

Chalmers, for tin, and Hanffstengel and Hanemann, whose results are shown in Fig. 12, for lead, found that the transition from viscous flow

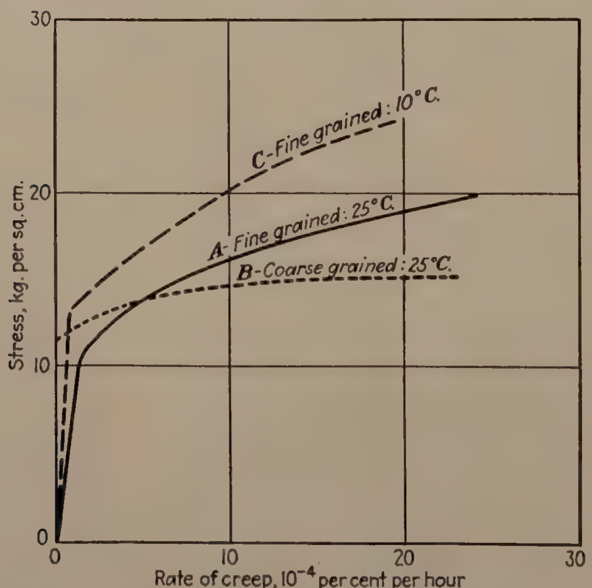


FIG. 12.—CREEP RATE-STRESS CURVES FOR LEAD (HANFFSTENGEL AND HANEMANN).

to plastic flow as the stress is increased occurs rather abruptly, while the latter workers have noted a similar abrupt change in the form of the

creep rate-temperature curve under constant stress as the temperature is increased.

For higher stresses the plastic flow is better expressed by a power function of the form

$$V = kS^n$$

In this equation the power exponent varies over a moderate range with temperature and stress, so that the law of plastic flow is only approximate.

An exact mathematical analysis of the shape of the stress-rate and elongation-time curve is probably impossible at the present time, owing to difficulties in testing and variation in materials. Nevertheless, there is strong evidence indicating the probability that at very low stresses the mechanism of deformation and the mathematical expression of the flow relation differs materially from those existing under higher stresses.

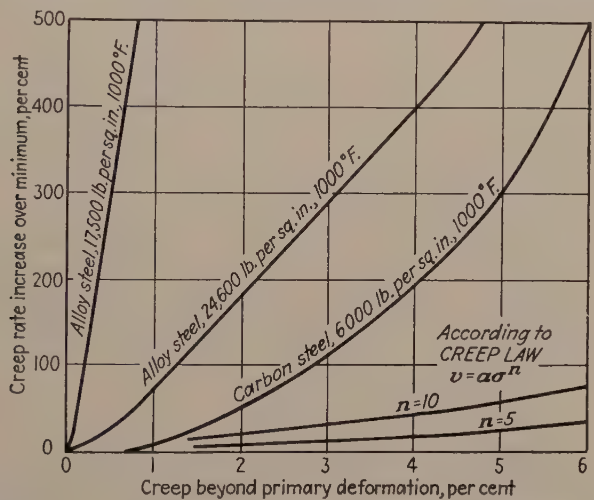


FIG. 13.—COMPARISON OF ACTUAL ACCELERATION OF CREEP RATES WITH ACCELERATION DUE TO REDUCTION OF SECTION (KANTER).

ACCELERATING CREEP RATE

In the history of any specimen stretching under a constant load, the final stages must consist of an accelerating strain produced by the decreasing cross-sectional area of the specimen. It is a simple matter to calculate the average stress intensity during creep as the metal extends; the rate of extension at any moment due to stress intensity can be calculated from the law of plastic flow, using appropriate values for the power exponent of stress. Such calculations, due to Kanter,[7] are shown in Fig. 13, using values characteristic of the range observed for steel, together with the results of tests carried out by White, Clark and Wilson.[16] The creep rate is seen to progress at a much higher rate than can be accounted for by reduction of area. Two things are clear from this

diagram; namely, that the time during which the minimum creep rate is maintained is much less than can be accounted for by the change in dimensions of the material, and that a factor must be introduced representing a change with time in the quality of the material, a change that is very substantial when measured in terms of creep rate.

This quality factor is commonly assumed to be the more rapid onset of recrystallization as extension proceeds, and this is without doubt true in certain instances. There are many cases in which this explanation is unsatisfactory, as I hope to show, and other reasons must be sought. Tapsell[17] has expressed the opinion that creep accelerates at the moment cracking begins; Wheeler and I[18] have produced evidence to show that in single crystals of aluminum the onset of acceleration is accompanied by a change in the mechanism of flow and probably by the beginning of fracture; Kanter[7] has referred to the possibility of grain rotation giving rise to preferred orientation. The investigation of this stage of creep may be considered unimportant from the practical point of view, since stresses coming within its range are undesirable in practice. I believe this view to be ill-founded, partly because within this range is the explanation of creep fracture to be found, and partly because behavior within this range, being caused, as we have seen, by a change in quality during the preceding stage, is related to the earlier history of the material. A study of deformation within this range, which is comparatively easy owing to the magnitude of the changes involved, may well afford a clue to the nature of the movements taking place at an earlier stage in which the smallness of the dimensional changes makes investigation rather difficult.

Relation between Stress and Minimum Rate of Creep

The correlation of creep results is a matter of some difficulty; tests are commonly carried out by subjecting a metal to constant loads of different amounts at the same temperature, the rate of strain being measured from time to time during the test. The creep rate-time curves are under these circumstances only qualitatively similar, and no simple method of expression is known which will take account of all the variations in behavior under load. Some method of correlation or analysis is however essential in applying the results of creep tests, if only for the reason that the time taken to carry out creep tests usually limits the number that can be made for any particular purpose. Interpolation is commonly needed to arrive at comparative figures for different materials, or for the same material at different temperatures, while, for the purposes of design, extrapolation is often necessary to periods far exceeding that of any reasonable tests. For both these purposes, but particularly for extrapolation, it is desirable to use some quality of the material that can be expressed as a definite function of load and time.

For this purpose the minimum creep rate or the rate of uniform flow is clearly the most convenient property. This method of analysis suffers from two rather serious drawbacks, although it has the advantage of being represented by a fairly well-defined law over wide ranges of stress. The creep rate-stress curve does not give a measure of the total amount of creep within a specified time because it fails to take account of the increased rate during the early period of the tests, where this exists. Where total elongation is important, as it is in many instances, that occurring during the primary stages must be estimated and allowed for. A second difficulty arises from the fact that, particularly with small rates of strain, the time taken to attain the minimum rate may be very long, and even exceed the time commonly allotted to lengthy tests. Instances have been recorded in which true minimum

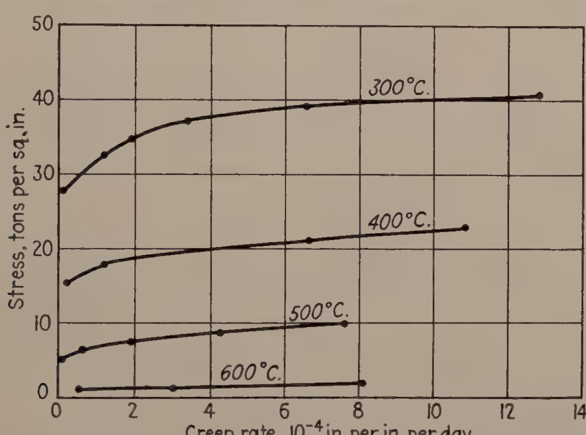


FIG. 14.—VARIATIONS OF CREEP RATE WITH STRESS IN A CARBON STEEL (TAPSELL).

rates were not developed even in tests of 40 to 100 days duration. The difficulty here is perhaps not so great in practice, if due care is taken, for it may reasonably be assumed that the rate measured at the end of the test will not be exceeded for a very long period, if at all. There is, however, a danger in the use of points obtained in this manner for the determination of the shape of curves which have to be extrapolated to endurances greatly exceeding the period of the test. There is in addition the possibility which I have indicated that at low stresses the law of plastic flow may no longer hold.

Fig. 14 shows the form of the curve connecting stress and minimum rate of creep when the two are plotted directly. They indicate the rapid decrease in the creep rate as the stress decreases. Such curves are clearly not suitable for extrapolation in the absence of any clearly defined relations and even interpolation is not safe unless the curve is determined by an adequate number of experimental points. The obvious advantage

of a well-established natural law which would enable the form of these curves to be determined by two or three experimental points does not need emphasizing in connection with such a time-consuming operation as creep testing. The method of double logarithmic plotting is perhaps the most commonly used for the presentation of creep-rate data, and results so plotted frequently appear to lie well on straight lines, especially when the range of creep rates is not very great. On the other hand, equally satisfactory results appear to be given in other instances by plotting the stress against the logarithm of the rate of creep; both of

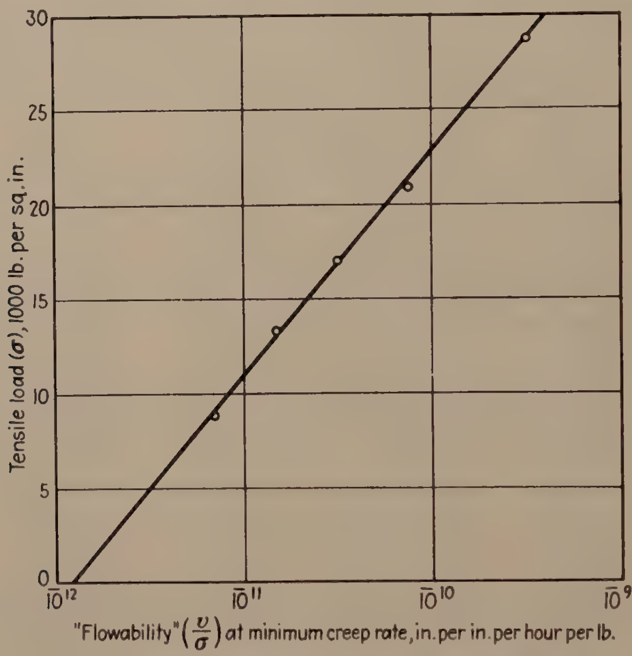


FIG. 15.—STRESS VERSUS FLOWABILITY, SEMILOG PLOT.

these methods appear to fail at low and high rates of strain (Tapsall,[17] Nadai[19]). Kanter[7] represents the change in the minimum rate of creep with stress by introducing the idea of a changing viscosity. In the initial stage flow is considered to be purely viscous and is determined by the primitive coefficient of viscosity of the original material: during the period of decreasing rate under constant stress the effect is equivalent to a rise in the coefficient of viscosity. The actual rate at any moment then depends not only on the stress but on the instantaneous value of the coefficient of viscosity. The factors governing this instantaneous value are doubtless complex, and are probably determined largely by the balance between strain-hardening, recovery and annealing. Continuous flow at the minimum rate at constant stress implies a constant value for this coefficient. Kanter has plotted the load against the logarithm of the

flowability at the minimum creep rate, as shown in Fig. 15. The flowability, which is the reciprocal of the viscosity, is a function of stress and creep rate $\left(\frac{\text{rate of flow}}{\text{stress}}\right)$. This curve, which takes account of the change in viscosity, may prove to give a more satisfactory correlation of creep rates, and to take account of the flow at low creep rates. It represents a behavior in which the viscosity decreases in geometrical proportion to the stress. Kanter describes this as "quasi-viscous flow" and suggests that a relationship of this kind represents creep under all stresses and in particular gives a rational interpretation of creep at very small stresses.

Determination of High-temperature Strength

It is clear that the determination of useful strength at elevated temperatures is a matter of considerable difficulty, as any possible figure for strength only has significance when associated with deformation and time. A complete picture of the behavior of a material requires for each temperature a three-dimensional chart expressing the effect of these variables. One of the principal difficulties in applying results of creep tests is the need for extrapolation far beyond the time occupied in testing. This commonly involves assumptions as to the future course of the creep-time curve which it is not always possible to justify. Estimates of future behavior usually assume that some specified rate of creep, generally the minimum measured in the tests, will continue indefinitely. The development of a steady rate of flow during the test implies that at some future time this rate will accelerate; it is not possible to say exactly when that moment will occur, although experience is gradually building up a background of knowledge upon which reasonably safe estimates may be based. French,[4] working on a 0.24 per cent carbon steel, found that the product of the duration and some power of the minimum rate was a constant. His duration did not exceed 20 days. Tapsell[17] confirmed that this relation was approximately true for Armco iron and a number of steels for durations up to 100 days. Some of these results are plotted in Fig. 16.

Without attaching too much importance to the linearity of this relation, the curves do appear to offer some justification for the assumption that minimum creep rate of 10^{-5} inch per inch per day or less will be associated with a long life of many years. There should, however, be evidence that the material will not develop brittleness to such an extent that it is unable to sustain this prolonged rate of creep.

In practice, measurement of creep at the minimum rate is not always simple. In the higher ranges of temperature minimum rates may be comparatively easy to determine, for they usually occur at a comparatively early stage in life, even under comparatively low loads in the neighborhood of the limit of proportionality as determined by the normal rapid test. In such an instance the rate of creep will inevitably increase

and lead to ultimate failure; the estimation of a probable life is therefore difficult. At the other end of the temperature scale, the minimum creep rate is developed but slowly, and may not even have been attained at the end of tests lasting 50 days or more. The minimum rate measured during the tests will thus be greater, possibly much greater, than the true value. Estimates of life based on such tests are conservative and safe, but the method is not, of course, ideal for the estimation of stresses for design purposes.

Numerous attempts[20,21] have been made to obtain creep data for design purposes by means of tests occupying a few days, or even hours.

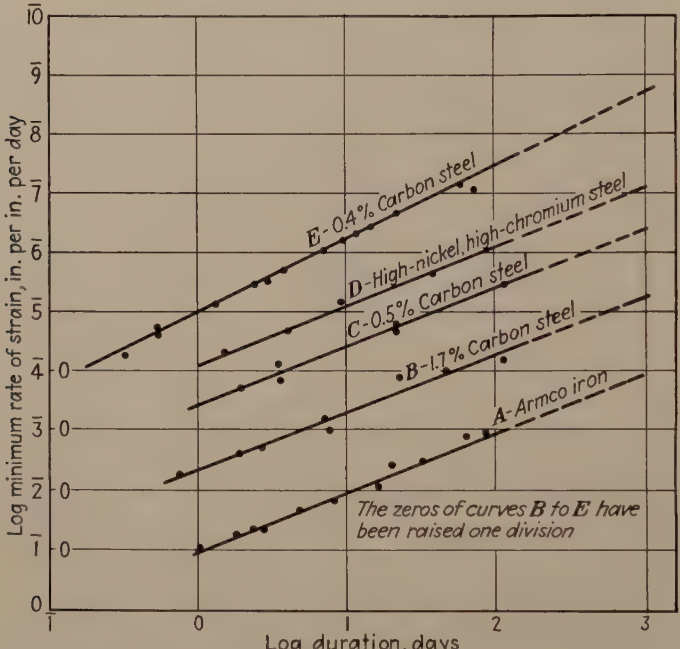


Fig. 16.—Strain-time curves, log-log plot.

These methods usually require that a certain minimum rate of strain must not be exceeded during a specified period in the early life of the specimen, and sometimes, as in Hatfield's[36] time-yield test, a maximum permissible total primary extension is defined. Such methods are worthy of much further study, as any reliable test of this kind would have the greatest practical usefulness on account of the saving in time which would result. It is, however, not likely that any great success will be achieved in this direction until much more is known of the form of the various curves representing long-time tests, and much more must be done in the careful study of creep by reliable tests of long duration, extending to several thousand hours. For the present the most useful

tests are those of long duration, which will enable reliable diagrams to be prepared giving the estimated amounts of strain associated with variations in time, temperature and stress. Such a diagram is shown in Fig. 17, incorporating results by Kanter and Spring.[22,23]

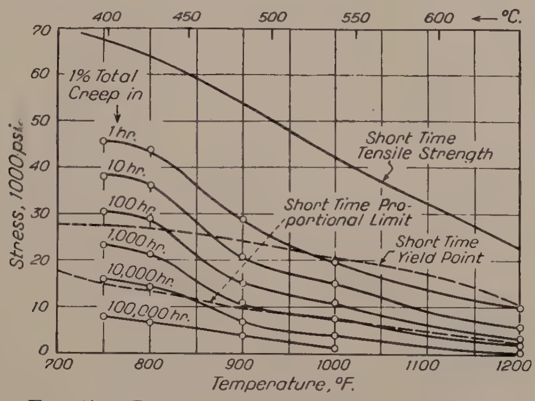


Fig. 17.—Results by Kanter and Spring.[22,23]

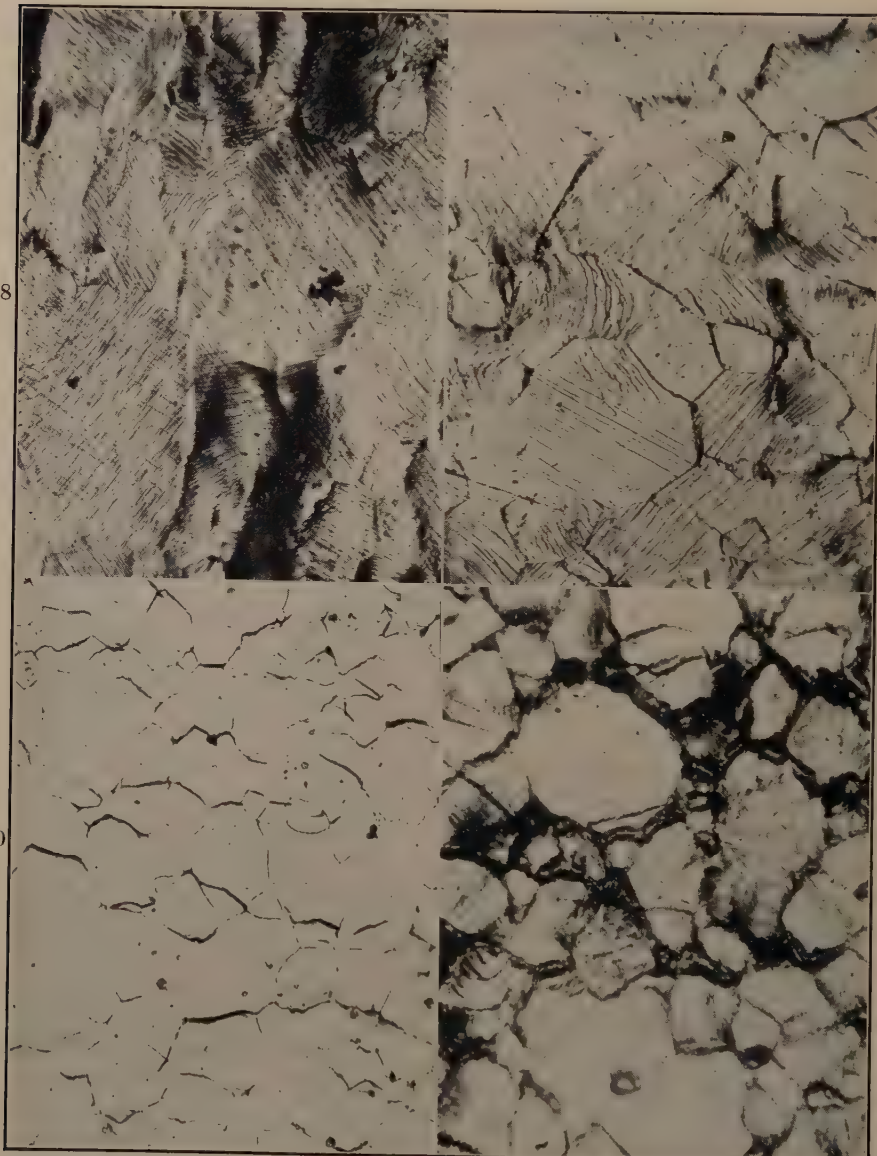
Metallographic Study of Creep

Although there is now a very considerable literature dealing with the creep of metals, most of the investigations so far undertaken have dealt with the determination of stress-strain-time relations and their utilization in industry. This is only to be expected in view of the great industrial importance of this question. The mechanism of flow and fracture has been little studied, and there are therefore many features of the behavior of metals under prolonged loads which are as yet improperly understood. It is, of course, well known that in general when metals are strained they become harder and stronger, and that this increase in hardness or strength can be wholly or partially removed by heating them to elevated temperatures. The main features of strain-hardening and annealing are familiar to all engineers and metallurgists, and it is natural that attempts should have been made to explain creep on the basis of a balance between these two opposing effects.

It is now well known that the distortion of metallic crystals takes place by shear in certain crystallographic directions. Slip is controlled by the resolved shear stresses in these directions and usually involves movement of one crystallographic plane over another. The movements do not consist of a uniform shear of the crystal, but are confined to relatively few planes in any one crystallographic direction, thus giving rise to distortion by the movement of blocks of metal over one another. The number of such planes taking part in the distortion is usually small compared with the number of similarly orientated planes in the crystal, and is approximately proportional to the stress producing the distortion.

One of the most interesting methods of studying the distortion produced in metals when they are deformed is that devised by Rosenhain,

18 19



20 21

FIG. 18.—SLIP-BANDS IN ALUMINUM, PRODUCED AT ORDINARY TEMPERATURE. × 150.
FIG. 19.—SLIP-BANDS IN ALUMINUM, PRODUCED AT 250° C. × 150.
FIG. 20.—ALUMINUM EXTENDED 4 PER CENT IN 20 MINUTES AT 250° C. × 150.
FIG. 21.—SAME AS FIG. 20, FURTHER EXTENDED TO 21 PER CENT IN 210 HOURS. × 150.

who prepared the surface of his specimens with a metallographic polish. It was by means of this technique that he discovered the slip-bands and

demonstrated the deformation of metals by block movement. Other changes in the metal are also capable of producing surface effects, and the method has obvious limitations, but it appeared to me to be worth while to apply it to the study of the phenomena of creep. One of the most serious difficulties in this connection is the deterioration of the polished surface at the working temperature, and the protection of specimens by using them in a vacuum or special atmosphere is not easy. Aluminum is one of the few metals on which the metallographic polish can be preserved free from substantial oxidation over the range of temperature in which creep phenomena are well marked. It can also readily be obtained in the form of single crystals. For these reasons it lends itself very well to metallographic studies at elevated temperatures.

Wheeler and I[18] strained polished specimens of pure aluminum at various rates at ordinary and elevated temperatures, and studied the nature of the deformation by means of changes in the microstructure. We were able to distinguish methods of flow and fracture which varied widely in their characteristics according to the conditions of the test.

When aluminum is strained at ordinary temperatures at the rate commonly used in mechanical testing the slip-bands have the appearance shown in Fig. 18. In annealed metal they appear at low stresses when the elongation is less than 1 per cent, and the number increases approximately in proportion to the stress. They are normally very distinct and well marked, and the apparently undistorted blocks into which they divide the crystal are very wide compared with the thickness of the slip bands themselves even when the total distortion is substantial. The mechanism of distortion appears to be substantially the same when the test is carried out at elevated temperatures, certainly up to 400° C. Fig. 19 shows slip bands in pure aluminum strained at the same rate by 21 per cent at 250° C. In both cases the crystals extend progressively as the test is continued and a normal transcrystalline fracture eventually occurs.

When the metal is extended more slowly at elevated temperatures the behavior is quite different; Figs. 20 and 21 show stages in the stretching of a similar sample under an initial load of 1.4 tons per sq. in. at 250° C. Fracture in this case ultimately occurred after 220 hr., the final elongation being 23 per cent. Fig. 20 shows the appearance after 20 min. under load, the elongation being 4 per cent. The crystal boundaries are well developed, but no slip-bands can be seen on the surface of any crystal. After 210 hr., the elongation then being 21 per cent, the appearance is as shown in Fig. 21. This elongation is identical with that of Fig. 19, representing a specimen strained rapidly at the same temperature, and the difference is remarkable. In the one structure slip-bands are the prominent feature, the boundaries being but moderately well defined, whereas in the other the crystal boundaries are very prominent and slip-bands almost or entirely absent. The specimen shown in Figs. 20 and 21

ultimately failed by intercrystalline cracking after 220 hr. under load. The appearance of this specimen suggests that intercrystalline cracking begins at an early stage in the history of the specimen, and indeed several workers have suggested that intercrystalline failure under creep may be the result of flow in the boundary material alone. This is certainly not true in the early stages of the deformation in spite of the absence of slip-band markings; we have frequently observed extensions of 4 per cent or more in the primary period of flow in which the deformation of the individual crystals are the same as that of the specimen as a whole; that is, they were elongated in the one direction and contracted in the other to the same degree as the test piece itself. Moreover, metallographic examination at this stage fails to reveal any signs of cracking, and if the surface of the test piece be repolished and re-etched a smooth surface free from fissures is obtained. The idea of distortion by movement of the crystals over one another without plastic flow in the crystals themselves cannot be accepted; the slightest movement of this kind at the boundaries would result in the complete disintegration of the whole material. Although the exact measurement of the distortion of each individual crystal becomes a matter of greater difficulty when the elongation is 10 per cent or more, owing to disturbances of the structure in the neighborhood of the boundaries, there is little doubt that each crystal distorts approximately as much as the specimen itself. The conclusion must therefore be accepted that substantial distortion of the crystalline matter can take place without the production of normal slip-bands.

An examination of the material in the immediate neighborhood of the boundaries reveals further differences between this type of distortion and that occurring by normal slip. Normally the slip-bands extend right up to, or at any rate very close to, the crystal boundary, and boundary effects do not usually extend very far. When aluminum is slowly strained at 250° C. the movements that reveal the positions of the boundaries are shown by high-power examination to be more complex in character. Fig. 22 shows a photograph at 600 diameters of a specimen which has been extended 8 per cent in 136 hr., repolished to give a smooth surface, and extended a further 1.2 per cent in 96 hr. The markings reveal movements due to this latter slow extension. The crystal boundaries themselves are smooth and clean-cut, when revealed by etching, and the surface markings in their neighborhood produced by slow flow are therefore considered to indicate complex distortions in the neighborhood of the boundaries rather than the position of the actual boundaries themselves. The appearance suggests a uniform distortion within the crystal grain and a more complex distortion for some distance in the neighborhood of the boundary.

22 23

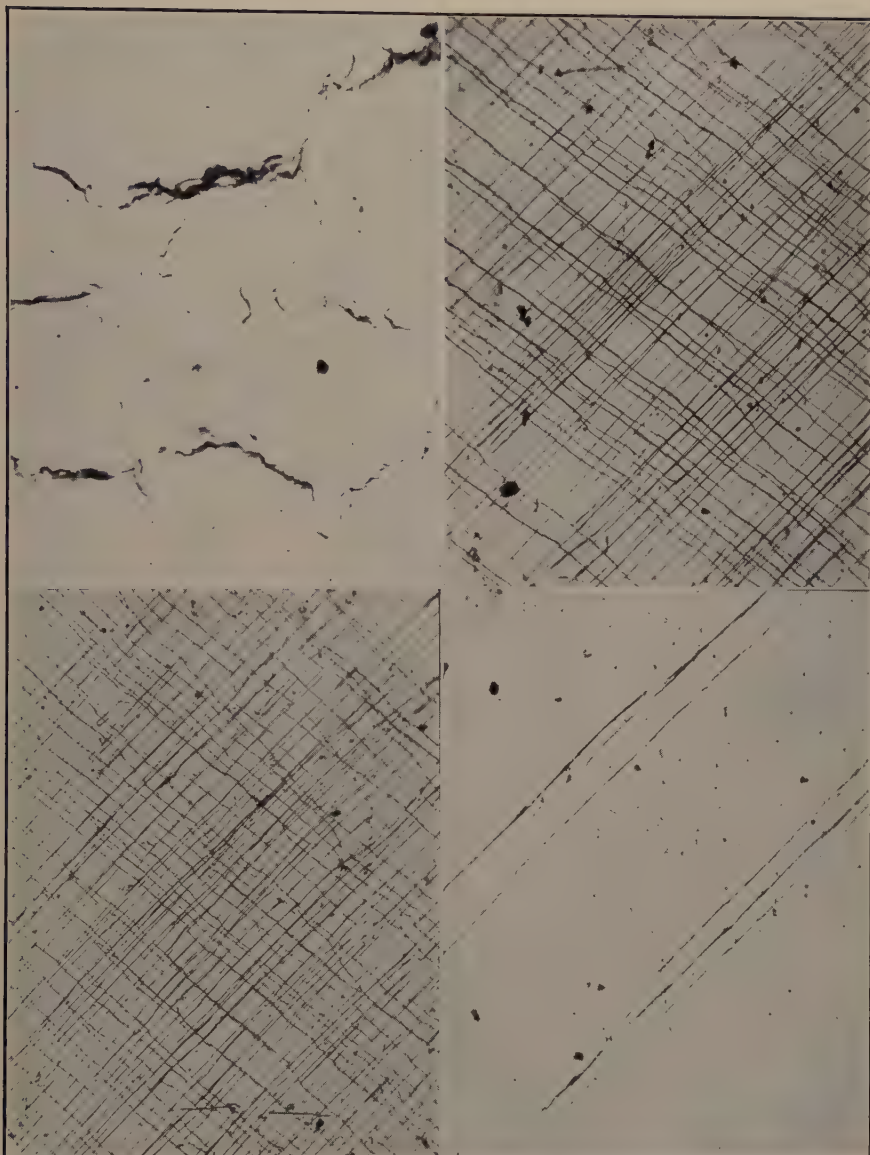


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FIG. 22.—ALUMINUM EXTENDED 8 PER CENT IN 136 HOURS; REPOLISHED AND FURTHER EXTENDED 1.2 PER CENT IN 96 HOURS. × 600.

FIG. 23.—ALUMINUM SINGLE CRYSTAL EXTENDED 8 PER CENT IN 41 HOURS AT 250° C. × 150.

FIG. 24.—SAME AS FIG. 23, FURTHER EXTENDED TO 10 PER CENT EXTENSION IN 252 HOURS AT 250° C. × 150.

FIG. 25.—SAME AS FIG. 24; REPOLISHED AND EXTENDED ANOTHER 0.6 PER CENT IN A FURTHER 400 HOURS AT 250° C. × 150.

In order to exclude the effects of boundaries, specimens of the same metal were tested in the form of single crystals prepared by the method of straining and annealing. When these single-crystal specimens were tested at 250° C. normal slip-bands were produced in profusion at rates of flow that produced no sign of slip in the crystal aggregates. Figs. 23 and 24 show stages in the extension of a single-crystal specimen at 250° C., Fig. 23 representing an elongation of 8 per cent produced in 41 hr. and Fig. 24 one of 10 per cent produced in 252 hr. The features are those produced in the normal rapid extension of single crystals at ordinary temperatures. In order to study the later stages of distortion and fracture this specimen was repolished at intervals to remove the surface defects due to previous extension, in order that those effects due to the later stages could be disclosed. Fig. 25 shows the same specimen as that illustrated in Fig. 24 repolished and loaded for another 400 hr., during which an elongation of only 0.6 per cent occurred. This is clearly the interval of the minimum creep rate. Fig. 26 shows the same spot after the specimen has been repolished and loaded for a further 48 hr., during which the specimen elongated 1.5 per cent. The accelerating flow had clearly begun before the end of the 400-hr. period by shear on a comparatively small number of surfaces; Fig. 26 shows that it continues mainly on these surfaces. Fig. 27 shows the same specimen repolished and reloaded for another 19 hr., after which fracture occurred with a total elongation of 37 per cent. The large distortion during the final stage of the experiment, amounting to more than two-thirds of the primary distortion, has been confined to comparatively few slipping surfaces. These heavy shear bands are not characteristic slip-bands; not only are they much more intense, but they do not exhibit the regularity of slip-bands, while they are also much more curved and are frequently forked. The two kinds of shear bands, the light slip-bands produced during the early stages and the heavy bands produced during the later stages of extension are shown together in Fig. 28, which represents a crystal slowly extended at 300° C. without repolishing until necking began. This photograph shows the relation between the two sets of bands rather clearly; the heavy bands appear to have originated in the light bands, for their directions coincide over considerable portions of their length. The heavy bands, however, pass from slip-band to slip-band, and their general direction differs markedly from that of the nearest system of slip-bands. The appearance suggests that, whereas the light bands are determined as to position by the crystallographic direction of the metal lattice, the general direction of the heavy bands is determined by other considerations, probably by the maximum shear stress.

In a further experiment a specimen composed of two crystals with a transverse boundary was broken at 250° C. in 658 hr. During the primary stage each crystal developed normal slip-bands of the straight

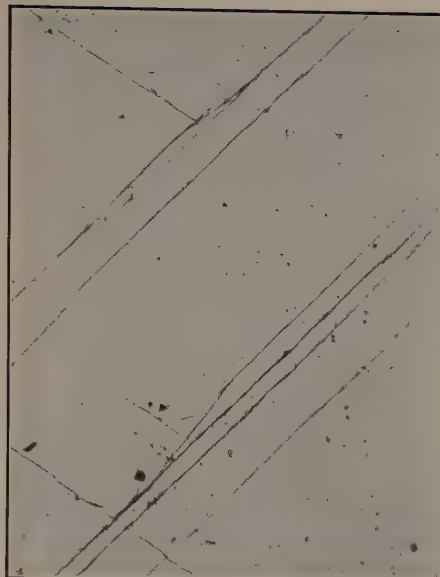


Fig. 26.

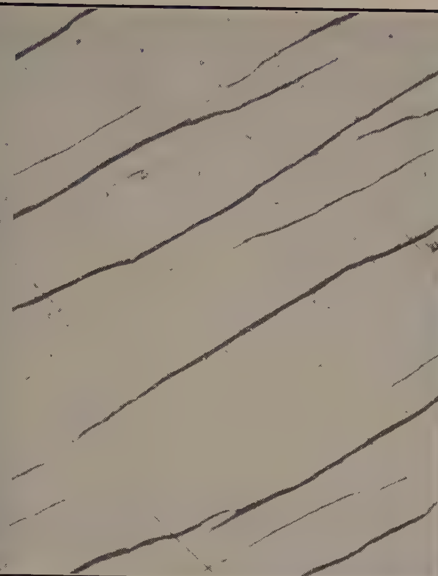


Fig. 27.

Fig. 28.

Fig. 26.—Same as Fig. 25; repolished and extended another 1.5 per cent in a further 48 hours at 250° C. × 150.

Fig. 27.—Same as Fig. 26; repolished and reloaded until fracture occurred in another 37 hours at 250° C.; total extension 37 per cent. × 150.

Fig. 28.—Aluminum single crystal slowly extended at 300° C. nearly to fracture without repolishing. × 150.

type characteristic of shear on octahedral plane. In places along the boundary, however, distortion markings of a more irregular type were detected, as shown in Fig. 29, which represents the structure at the end

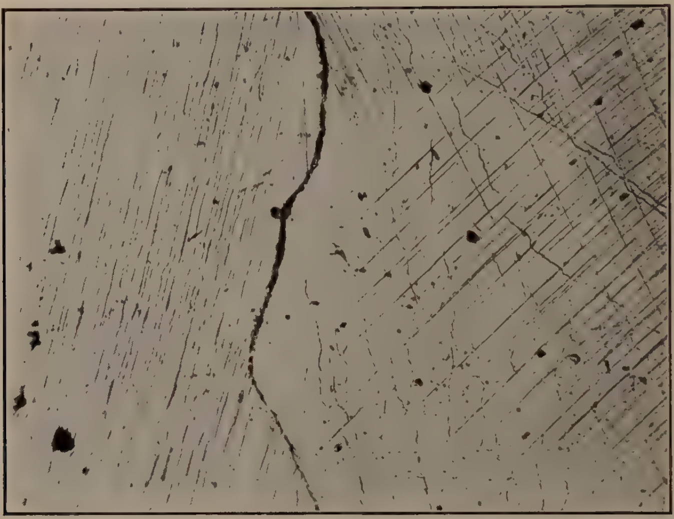


FIG. 29.—ALUMINUM TWO-CRYSTAL SPECIMEN. APPEARANCE AT TRANSVERSE BOUNDARY AFTER EXTENDING 20 PER CENT IN 252 HOURS AT 250° C. × 150.

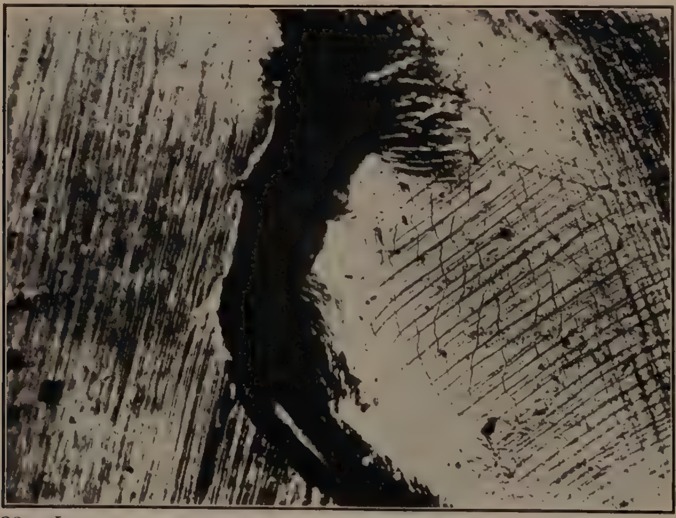


FIG. 30.—INTERCRYSTALLINE FRACTURE AT SPOT SHOWN IN FIG. 29. × 150.

of the period of declining creep (252 hr.). The extension at this stage was 20 per cent. This specimen remained substantially unaltered in appearance for a further 300 hr., after which a crack began to develop at the boundary. This crack spread about halfway across the section,

along the boundary, and rupture finally occurred rapidly by a tearing fracture through one of the crystals. The nature of the fracture is clearly shown in Fig. 30, which shows the two halves of the specimen placed side by side after failure had occurred.

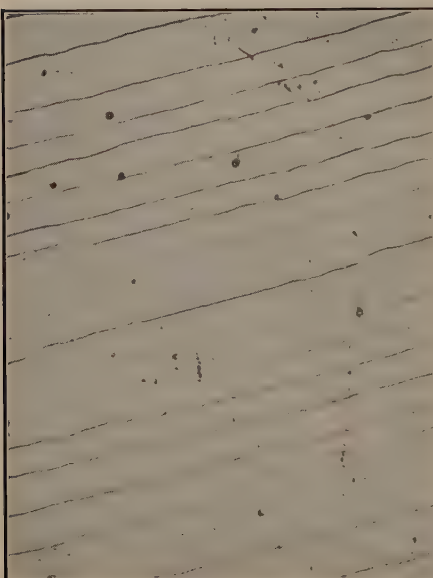
In another instance a specimen consisting of a single crystal containing a small included crystal in the center of one face was also tested at 250° C. In the early stages typical straight slip-bands appeared in both crystals, and this was followed by a period of some 400 hr. at the

FIG. 31.—INTERCRYSTALLINE CRACK AT JUNCTION OF MAIN AND SMALL INCLUDED CRYSTAL OF ALUMINUM AT 250° C. × 150.

minimum creep rate, during which no observable changes in its microstructure took place. After a total life of 480 hr. indications of failure were observed and the test was stopped. The acceleration of flow was found to be caused by the development of a crack starting from the boundaries between the small and the main crystal. This occurred at this point in spite of the fact that the cross section was here greatest, owing to the interference of the boundary. The crack between the crystals is shown in Fig. 31.

In view of the failure to demonstrate appreciable flow in single crystals without normal slip, a further series of experiments was undertaken in which the load was applied very gradually. These tests were carried out both at room temperature and at elevated temperatures up to 400° C.

Very slow rates of loading were adopted, resulting in creep at rates not exceeding about 0.1 per cent per day. When the load was allowed to remain constant for some days, rates considerably lower than this were observed. These rates are, of course, large compared with those normally used in creep testing, but they are small compared with rates often found during initial loading, when extensions of 1 per cent or more may occur during the first day. It was found that the character of the distortion could be altered profoundly by the use of a sufficiently slow straining rate. Under some conditions an extension of as much as 4 per cent



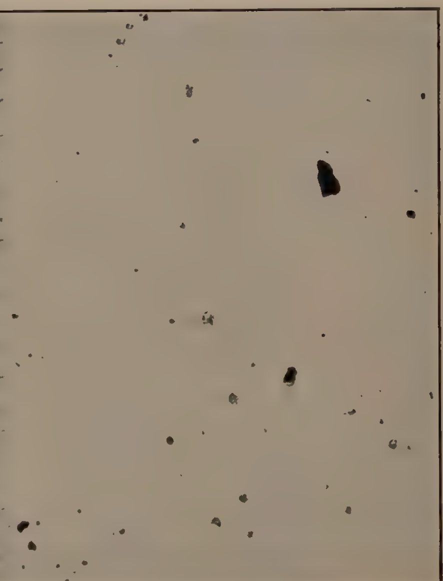


FIG. 32. FIG. 33.

FIG. 32.—ALUMINUM SINGLE CRYSTAL EXTENDED 0.9 PER CENT IN 2 MINUTES AT NORMAL TEMPERATURE. × 150.

FIG. 33.—ALUMINUM SINGLE CRYSTAL SLOWLY EXTENDED 1.8 PER CENT IN 52 DAYS AT 250° C. × 150.

could be obtained before any surface effects became visible. The general character of the results is illustrated in Figs. 32 to 35. The normal features of distortion produced by an elongation of about 1 per cent imposed in 2 min. either at ordinary or at elevated temperatures is shown in Fig. 32. Single crystals extended to this degree sufficiently slowly at room temperature, at 110°, 250° and 400° C. showed no sign of any surface effects whatever. At room temperature slip-bands became clearly visible before the extension reached 1.5 per cent, while at elevated temperatures surface features were not detected until the elongations were of the order of 2 per cent or more. Fig. 33 shows the surface appearance of a single crystal elongated 1.8 per cent at 250° C. in 52 days, at the

average rate of about 0.04 per cent per day (the instantaneous rate must at times greatly have exceeded this rate). The surface markings are hardly to be seen in the photograph, since they are so slight, and they required for their detection careful manipulation of the lighting and focus, which has greatly exaggerated the size of the particles of impurity in the metal. Faint striations however can be seen, suggesting a slight rumpling of the surface. Nothing like normal slip-bands is visible. Fig. 34 shows similar markings produced in a single crystal slowly extended 2 per cent at 400° C., the rate being slightly greater than 0.1 per cent per day. Close to one end of the parallel portion of this test piece there

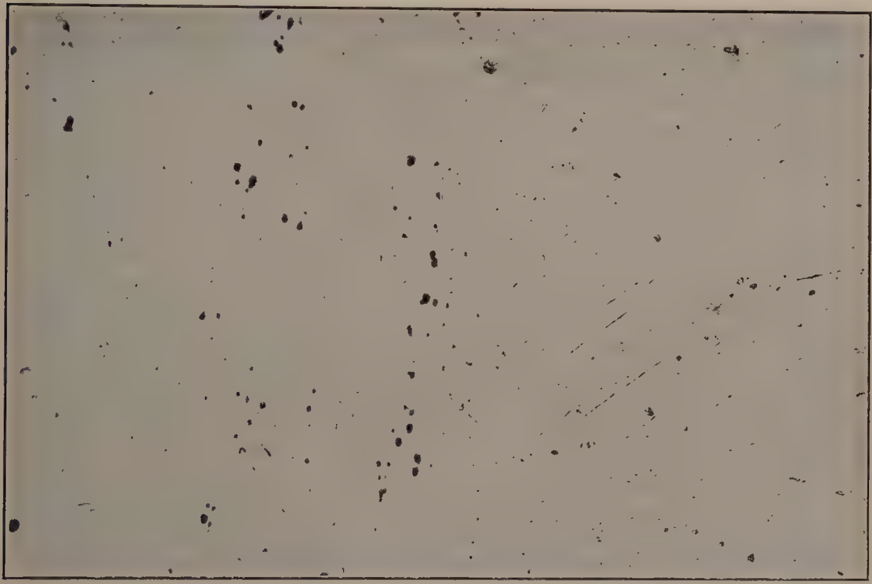


FIG. 34. FIG. 35.

FIG. 34.—ALUMINUM SINGLE CRYSTAL EXTENDED 2 PER CENT IN 13 DAYS AT 400° C. × 150.

FIG. 35.—ALUMINUM SINGLE CRYSTAL EXTENDED 4 PER CENT IN 216 DAYS AT 110° C. × 150.

was an exceedingly small crystal included in the larger crystal; the boundary between the two became extremely well developed long before any sign of visible deformation could be detected within either crystal. No signs of recrystallization could be detected, although the specimen was under load for a period of 17 days at 400° C., a temperature greatly exceeding the normal minimum recrystallization temperature. Fig. 35 shows a specimen extended 4 per cent at 110° C., the rate being much slower, namely, 0.01 per cent per day. Traces of normal slip-bands can just be detected. In spite of the lower temperature, the use of a lower rate of straining has permitted a greater extension to be obtained without signs of visible slip-bands.

It is clear that no single mechanism can explain all the features of creep. In addition to those already described, there is the mechanism of flow and failure through continuous recrystallization; that is, a continuous formation of new undistorted crystals. Such a mechanism has been described by Beckinsale and Waterhouse[24] for lead at ordinary temperature, by Clark and White[11] for certain brasses above 300° C., and by others. The onset of recrystallization is accompanied by abnormally rapid rates of flow, and a period of declining creep is probably absent. The metal gradually extends until it fails with very large elongations and a point fracture, as would be expected if the metal is being automatically returned to its original annealed condition. For lead Beckinsale and Waterhouse[24] state that creep begins by slipping within the crystal, but when the amount of strain thus produced exceeds a few per cent recrystallization of the metal occurs and flow becomes rapid; cycles of hardening and recrystallization succeed one another until the metal draws out to a point and breaks.

Types of Flow and Fracture

We are now able to recognize that flow and fracture may take place in a number of different ways.

Flow may occur: (1) by normal slip, involving shear on crystallographic surfaces widely separated from one another, (2) by a more uniform distortion, which we may call "slip-less" flow,* (3) by the continued primitive distortion of new crystals continuously produced by recrystallization, (4) by movements at or near the grain boundaries.

Fracture may occur: (1) by gradual breakdown of the crystal (transcrystalline fracture), (2) by gradual breakdown of the crystal boundaries (intercrystalline fracture), (3) by the continuous drawing down of recrystallizing metal to a point fracture.

It is not yet possible to express any final opinion regarding the significance of these observations in relation to creep testing and the behavior of metals in service. Indeed, it is possible that other mechanisms of flow and fracture may exist of which we are as yet unaware. Moreover, nothing has yet been done to discover the differences, if any, associated with different mechanisms, or to ascertain to what extent some of the apparent anomalies in creep testing can be accounted for by different types of flow. Nevertheless, some speculations may be permitted in a lecture of this kind, in the hope that they may lead to the opening up of new lines of attack on this difficult problem.

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* It is difficult to find a satisfactory term to describe this flow. Further study may show that it is essentially the same as normal distortion in which the shear is spread over a large number of planes, but is nowhere sufficient to be detected by optical methods.

Deformation by Normal Slip

Deformation by the normal process of slip appears to occur most readily: (1) the lower the temperature, (2) the more rapid the rate of strain, (3) the larger the grain size.

The experimental evidence on these points is scanty, and certainly does not justify generalization, but it certainly points in these directions. In regard to the third point, it has repeatedly been observed that in test pieces containing large and small crystals side by side normal slip-bands occurred in the large crystals but not in the small crystals, although each size was strained to the same degree.

This type of distortion appears to be characterized by (1) strain-hardening and (2) a decreasing rate of flow. It appears to occur during the primitive flow associated with loads which cause comparatively big primitive extensions, and also with flow during the early part of the declining creep rate when the primitive flow is large. It is, in fact, associated with cold-working, in the ordinary sense of that term. This type of flow is followed by (1) the complete cessation of slip, which is probably favored by a comparatively low temperature, (2) slip-less flow, (3) recrystallization, favored by high temperature and high stresses.

The effect of distortion of this kind on the crystal structure has not been much studied for slow rates of creep; since the metallographic features are so similar to those associated with rapid flow, it appears justifiable to assume, for want of better evidence, that the crystal structure is affected in the same manner, and recent work by Moore[25,26] and his co-workers appears to support this view in the case of lead. Earlier investigators have not usually dealt with the effect of small distortion of the order of 1 per cent, although the inference has always appeared to be justified that slipping, even in its early stages, produces fragmentation of the lattice along the site of the slip-band, the fragments being rotated through small angles about the slipping plane. In my laboratory we have recently detected distortion of this kind associated with slipping in aluminum when the elongation was much less than 1 per cent. Further distortion adds to the amount of fragmentation, but does not appreciably alter the size of the fragments themselves. The degree of fragmentation produced by normal slipping in an early stage of the deformation appears therefore to be substantially the same in general character as that produced at a later stage, and to represent a profound local disturbance of the crystals.

Slipless Flow

Plastic flow without *visible* slip-bands appears to be the more readily produced: (1) the slower the rate of straining, (2) the higher the temperature, (3) the smaller the grain size.

In regard to the first item, there seems to be some evidence that the change over from one type of distortion to the other takes place rather suddenly at a critical straining rate. The mechanism involved in this type of deformation is not known, and any comments as to its nature or the processes involved must therefore be speculative. There is at present no real justification for assuming that it differs from normal slip except in the spacing of the surfaces of movement, for it may well be caused by shear of the same nature as normal slip, in which the movements are outside the resolving power of our microscopes.

It may, however, be of some interest to examine the possibility of a modification in the form of crystal distortion when effects due to time and increased temperature have greater opportunities of taking place than in rapid testing. There is ample evidence that distortion of comparatively small amounts sets up a condition of internal stress, and that the stresses produced by quite a small distortion may be considerable in their intensity. This is revealed by the loss of elasticity caused by overstrain, and by "elastic afterworking" or relaxation. The presence of internal stress is also indicated by the X-ray examination of deformed metals. When the straining is comparatively rapid, the existence of such internal stresses is likely to lead to a resumption or continuance of flow in those localized regions where the shear stress is at a maximum, and it may be that causes of this nature are responsible for the intense local shears which produce the slip-bands. These internal stresses gradually disappear at ordinary or slightly elevated temperatures during the process of "elastic afterworking."[27] Time may operate in this way against the intense localization of distortion associated normally with slipping, thus leading to a more uniform distribution of the distortion, which is in consequence invisible to our microscopes.

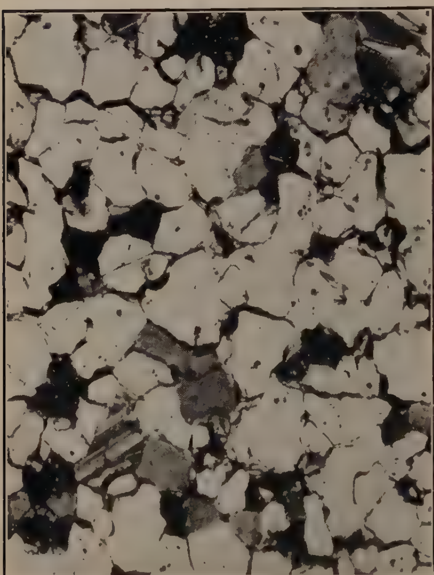

Fig. 36.—Zinc extended 25 per cent in 125 hours at 150° C. × 150.

The more uniform distribution of the distortion throughout the crystal might be expected to produce a greater hardening effect for the same total amount of distortion than when the shear is localized on widely spaced surfaces. On a number of occasions I have observed that the hardening effects produced by small distortions under creep conditions is

greater than that produced by a similar total distortion imposed rapidly on the metal.

The uniformity of the distortion throughout individual grains is well illustrated by Fig. 36, which shows a polished unetched surface of a zinc test piece extended 25 per cent in 125 hr. at 150° C. The crystals have rotated in relation to one another, but in spite of a very large distortion each crystal possesses a perfectly plane, polished surface except very close to the boundaries. This is well shown by the variations in tone between different crystals, which is entirely due to optical effects caused by varying degrees of departure from normality to the incident light.

The possibility that movements of a viscous character contribute to "slipless flow" cannot be excluded, although there is ample evidence that the movements cannot wholly be explained by purely viscous phenomena. The work-hardening sometimes associated with very slow distortion requires an internal change in the crystal itself; but it is quite possible that in the higher ranges of temperature the "viscous" factor predominates.

Effect of Temperature

The principal effects of temperature on cold-worked metal, apart from constitutional changes, are as follows: (1) to reduce internal stresses, (2) to induce softening, (3) to set up recrystallization. These effects, which can be separated from one another theoretically, in practice have overlapping ranges to an extent which varies considerably from metal to metal. They succeed one another in the order given as the temperature is raised. But they all require time for their completion, and the time involved decreases rapidly as the temperature is increased. Most of the practically important creep phenomena are associated with time-temperature conditions which do not produce recrystallization in the normal sense. Heating to an appropriate temperature will, without causing recrystallization, bring about more profound changes than the removal of internal stress: these changes are commonly classed together under the term "recovery" or "healing," but they are imperfectly understood. The hardness due to working is reduced, though not usually to the value for fully annealed metal. Recrystallization does not take place in the sense that new crystals are formed comparable with those in annealed metal, although the small grain fragments tend to rotate backwards towards their original orientation. When the processes of working and heating or recovery take place together slowly it is to be expected that internal stresses of a high order will never develop, nor will severe local distortion of the crystalline structure occur to the same degree as when the process of working is carried out in the cold. There is no evidence to contradict the assumption that distortion of crystals at elevated temperatures takes place by shear in crystallographic directions in the same manner as normal cold-working. The work of Miller[29] on zinc and of

Baker, Betty and Moore[26] on lead point clearly to crystallite formation in the creep range of temperature. Recovery appears to remove most of the hardening or strengthening effect of deformation while preserving most of the grain fragmentation. Without committing oneself to any particular theory of distortion, it is not difficult to imagine conditions under which this might lead to the limitation of slip on one plane to a small amount and to further distortion taking place in regions of the crystals in which fragmentation has not yet occurred. Wheeler and I have observed, in regard to single crystals and aggregates in aluminum and aggregates in zinc, that metals can be extended at high temperatures without recrystallization taking place, to a degree much greater than is possible if the processes of deformation and heating are carried out separately. If, as seems likely, the onset of recrystallization requires that the local distortion at some point must exceed a certain threshold value, it seems quite possible that under appropriate conditions of temperature a metal could extend gradually to a very considerable extent without any signs of recrystallization. I have observed distortions exceeding 25 per cent in zinc at 150° C. without recrystallization; and Baker, Betty and Moore[26] report that in lead crystals, which extended by more than 40 per cent at room temperature, recrystallization occurred only near to the fracture, where the metal was "very severely distorted," but not away from the break.

The existence of a threshold value for recovery has been suggested by Tammann[30] and by Hanffstengel and Hanemann.[14] A certain minimum distortion must therefore be exceeded before recovery can begin; this quite possibly corresponds to the critical point found by Chalmers[13] in tin and Hanffstengel and Hanemann[14] in lead at very low distortions.

The existence of a recovery threshold implies permanent strain-hardening and would lead to declining rates of flow under low stresses incapable of exceeding this amount of distortion.

The metallographic evidence which I have obtained in many experiments, which has recently been confirmed by Moore and his co-workers, strongly suggests the association of what I have called "slipless flow" with the period of constant creep rate.

Flow with Recrystallization

This type of flow probably occurs only with comparatively high stresses and comparatively large deformation. It is well known that a deformation threshold exists for recrystallization, the minimum deformation being the less the higher the temperature. Normally, deformation of the order of 1 to 2 per cent at ordinary temperature produces recrystallization only at high temperatures outside the practical creep range. Flow with recrystallization, therefore, can hardly enter into practical

creep phenomena except when comparatively high distortions can be permitted.

Recrystallization continually restores the crystals to their primitive condition of minimum elasticity; thus, any stress that causes extension in excess of the recrystallization threshold corresponding to the temperature involved must lead to a continual softening of the material, accompanied by continuous extension; since appreciable work-hardening is never imposed on the material, fracture in the normal manner due to the exhaustion of ductility does not take place, and the metal extends to a point fracture with high elongation. The form of the creep-time curve is accelerating, but it may take a complex form owing to cycles of temporary crystal distortion, up to the threshold value, followeg by recrystallization.

The existence of a threshold value is well shown by the following experiment due to Hanffstengel and Hanemann.[14] Two samples of lead were extended by 0.4 per cent and 2.3 per cent, respectively, and then subjected to a load of 228 lb. per sq. in. Creep curves are shown in Fig. 37. The form of the curve shows the very great increase in the rate of flow while recrystallization is in progress. Since 2.3 per cent is only just above the minimum effective extension, the onset of recrystallization is slow, and as the process depends on nuclei formation some time must elapse before it attains a maximum. When recrystallization is complete the rate of flow again diminishes. Experiments by Russell[28] in which the recrystallization took place more quickly confirmed this great increase in creep rate during recrystallization.

Flow at Grain Boundaries

Observations by many workers have shown that creep depends in part on processes taking place at the grain boundaries. The nature of the boundary is as yet little understood, but it is clear that the atoms in this region are not so exactly located in relation to their neighbors as those in the interior of the crystal. In the creep range of temperature atomic movement due to thermal effects must be pronounced—otherwise the process of recovery could not occur—and the possibility of positional changes is greatest at the boundary owing to the enhanced positional mobility of the boundary atoms. No doubt there is a continual interchange of atoms between neighboring crystals, even if the mean position of the boundary does not greatly change. When atomic movements of this kind take place under the influence of a stress, they will on the average be most frequent in the direction tending to relieve the stress. Flow due to atomic mobility will occur therefore much as in an amorphous material. This movement cannot account entirely, or even mainly, for the observed distortion, since appreciable flow without fracture could occur only if the movement extended into the grains themselves. When we consider the

interlocked nature of the grain boundaries we can see that any unidirectional atomic movements must throw increased stresses onto the interlocking projections. Moreover, the rotation of the grains in relation to one another (as shown in Fig. 36), which is an inevitable result of flow by shear on crystallographic planes, must involve complex stresses in the region of the grain junctions. They can relieve themselves from these increased stresses by localized plastic flow, also in a direction controlled by the applied load. A continual redistribution of the localized stresses at the boundary due to repetition of this process can account for the observed effects.

Fracture

The study of the mechanism of creep fracture is beset by many difficulties. The examination of specimens that have broken completely does not as a rule lead to conclusive results, because the final stages of separation do not involve creep phenomena at all, but are rather characteristic of ordinary tensile testing: the metal frequently extends rapidly, by processes that may differ greatly from those leading to the initiation of the cracks, while the extension in this period being usually as great or greater than that occurring in the preceding stages, may easily obliterate any effects due to creep.

If we exclude those cases in which recrystallization occurs, the elongations of specimens broken in creep tests bear no relation to those occurring in corresponding tensile tests. In some cases, as when intercrystalline cracking occurs, the elongation may be much lower in the creep than in the tensile test, and in others, where recrystallization phenomena predominate, it may be much greater. Having regard to the fact that creep testing is carried out in a range of temperature where annealing effects of one kind or another are commonly present, it would be expected that uncommonly high elongations would be the rule. This is certainly not true, and in a very large number of instances, probably the majority, final elongations are rather less in creep tests than in tensile tests carried out at the same temperature.

It is quite clear that great importance attaches to the point at which fracture begins, and in the majority of cases this must be regarded as the point at which the stage of accelerated creep commences. The method of metallographic examination which I have used, particularly the experiments in which the specimen has been repolished at stages during the test, thus removing the effects of prior distortion, throw much light on the stage at which failure must be regarded as having begun. In my experiments the period of fracture can be fairly clearly separated by appropriate tests from the preceding stages. During the stage of constant creep the metallographic features change little and the changes in physical properties such as hardness and density are not measurable.

The onset of the third stage is accompanied by definite metallographic features, which intensify steadily into definite cracks—the heavy shear-bands in the single crystals and the intercrystalline flow in aggregates. Simultaneously the hardness increases in the single crystal, and the density decreases in the aggregates. This acceleration of flow can be clearly distinguished from the primary extension: the final stage is not a resumption of the distortion by which the metal first yielded, for it has its own characteristic features. Just as the long period under load during the constant creep stage is made possible only because the plastic deformation of the initial period has strengthened the metal, so it is impossible to escape the conclusion that the change in mechanism during the last stage is due to internal structural changes which have been occurring gradually during the period of steady creep; we cannot otherwise understand why, under the same constant stress, flow should first decrease almost to nothing and, after a prolonged period, accelerate continuously. And since the metallographic features of this period develop steadily into cracks, we must conclude that it is the period of failure of the metal. We have already seen that it is not due to the effects of reduced cross section: moreover, the formation of cracks is equally clearly not due to loss of ductility in the ordinary sense, for at the stage at which the rate of flow begins to increase the metal is still soft, and when tested in tension or by bending reveals a ductility not greatly less than the original metal.

We are faced with the apparent anomaly that the application of a stress which produces a strengthening effect on the metal when applied for a short time actually induces a definite weakening of the material when sustained for a prolonged period. It is, however, not difficult to reconcile the two effects, for the action of long sustained stresses of sufficient intensity appears to cause disintegration of the metal at those places where it must be supposed that the orientation of the crystal is most disturbed; i.e., at the grain boundaries, or on the surfaces where normal slip has already taken place. The process of breakdown of the metal under these circumstances must be clearly distinguished from slipping, which is a definite movement of translation. Slipping, in a perfect crystal, is a mechanism by means of which the metal avoids fracture. If the act of slipping did not produce fragmentation and localized crystal disturbance, rupture would not occur until the section had been reduced to very small dimensions. But the introduction into the crystal of surfaces of imperfection, such as those between neighboring crystals, or at the junctions of the fragments, renders possible what has been called by Becker[31] "thermal" deformation. This type of flow occurs when an elastic strain is superimposed upon the normal thermal vibrations of the atoms, which change their positions one by one in their attempt to escape from the applied stress. It is clearly likely to occur most readily at elevated temperatures, for the increased thermal vibrations of the atoms

would require a smaller external stress to produce deformation. In a wholly amorphous substance this might cause continuous flow, but in a metal the disregistry required to facilitate these movements is greatest on surfaces widely separated from one another by regions of almost undistorted crystal, in which thermal deformation cannot so readily occur, if at all. Such movements might well be imagined in these circumstances to lead to gradual development of cracks by the breaking of the cohesion bonds one by one, especially when the applied force is a tension tending to pull the atoms apart. If the regions of crystal disturbance contain initial defects or discontinuities in the nature of minute cracks, such as probably occur on surfaces of severe slip or at grain boundaries, the stress concentration due to those discontinuities is likely to cause them to extend by thermal flow under comparatively low stresses.

An explanation of this kind appears to account for the location of the movements that initiate the stage of fracture, which occur preferably at grain boundaries or on the surfaces of severe deformation caused by the primary slipping. Such an explanation is consistent with the development of cracks under low stresses in completely ductile material: for if material undergoing thermal flow of this kind is subjected to a more rapid deformation, even if thermal cracks have to some extent developed, higher shear stresses are imposed on the material which will initiate the alternative mechanism of flow in the less disturbed regions—namely, normal slip.

Thus we see that the surfaces of slip, and the grain boundaries, which commonly behave as the strongest regions in a crystal, have within them sources of weakness which may, under the appropriate circumstances, be developed into cracks.

Factors Affecting Creep Strength

One of the difficulties in connection with the correlation and use of creep data lies in the wide differences that occur in the creep results obtained by different workers using similar materials. These differences are not wholly due to the use of different testing methods or apparatus nor to any want of care in the choice of material or control of its quality as ordinarily understood. Rather is it an indication of the fact that the creep characteristics of a metal are influenced profoundly by factors that are comparatively unimportant in relation to mechanical properties at low temperatures. Engineering alloys are influenced at normal temperatures by the physicochemical and structural modifications which normally accompany the different processes of casting, fabricating and heat-treating these materials. The principal physicochemical effects utilized to increase strength in the cold are supersaturation and the retention of unstable phases: the principal structural effects are fineness of the constituent crystals and cold-working. These factors have less

importance within the creep range of temperature, for the very atomic mobility which permits gradual creep to occur renders unstable these features which make for increased strength in the cold. Supersaturated solid solutions and unstable phases gradually give place to more stable phases; finely divided structures coarsen by the coalescence of their particles through diffusion; the hardness due to cold-working is reduced by softening and recrystallization. But these effects on the creep characteristics are even more profound than is represented by the diminution

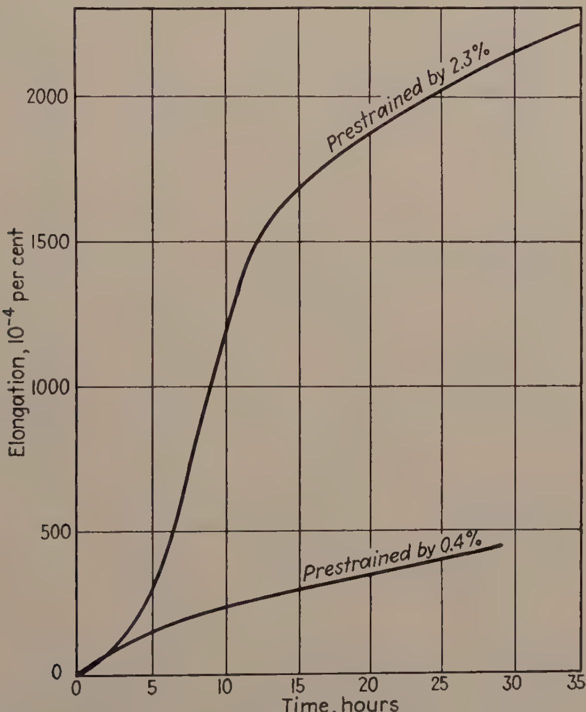

FIG. 37.—CREEP OF LEAD UNDER 228 POUNDS PER SQUARE INCH.

in tensile strength due to the internal changes which take place. There is now ample evidence to support the view that metals flow particularly easily *while internal changes are occurring.* Clark and White[11] found that creep in certain brasses became abnormally high while recrystallization was in progress, and that deformed steel[32] crept at 600° to 1000° F. more quickly while recrystallization was occurring than the same steel which had not been deformed. Beckinsale and Waterhouse[24] and Hanffstengel and Hanemann[14] find accelerated creep in lead and the latter workers state that "the creep rates during recrystallization are 10 to 20 times higher" than the rate of creep of the same metal prior to the onset of recrystallization (Fig. 37). Yamaguchi[33] finds abnormal

creep during transformations "when the microstructure changes." During such internal rearrangements, while the atoms are changing their positions, greater opportunity occurs for thermal flow of the kind to which I have already referred: when the changes in internal structure occur rapidly, as in the experiment by Hanffstengel and Hanemann described above, a comparatively large volume of the metal is involved at any one moment, and a great acceleration in the rate of creep might be expected: with other changes, such as gradual precipitation from a supersaturated solid solution or the coalescence of pearlite into globular cementite, the volume of metal at any moment concerned with the

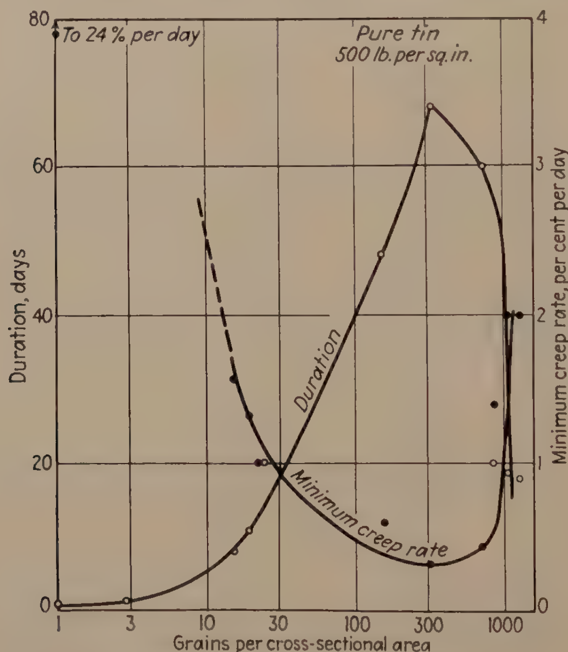

FIG. 38.—TYPICAL RESULTS FOR TIN.

change might be comparatively small, and the rate of creep correspondingly small.

If these views are correct, the most satisfactory type of alloying element will not be that which makes heat-treatment possible, but rather that which decreases the internal atomic mobility, and raises the softening or recrystallization temperature; while the most satisfactory heat-treatment will be that which produces the most stable crystalline structure.

Grain Size

The fact that grain size influences creep rate is well recognized.[10,11,12,17,34,14, etc.] Most of the workers that have examined this

property have used only a comparatively few grain sizes—often only two, described as fine and coarse, and no systematic study of the subject has yet been undertaken. Clark and White[32] have expressed the view that the influence of grain size changes at a definite temperature, which they call the "minimum recrystallization temperature" or "equicohesive temperature." Above this temperature a coarse-grained structure is superior while below this temperature a fine-grained structure possesses the greater creep resistance. Hanffstengel and Hanemann,[14] on the other hand, referring to lead, change the order at a critical point in the stress-rate curve (corresponding to a rate of the order of 10^{-4} per cent per hour). At rates of strain greater than the critical, the fine-grained lead creeps more slowly, and at lower rates the coarse-grained. Neither investigator appears to have measured the change in the rate of flow with change in grain size, and the generalizations appear to be premature. They cannot both be true for all rates of strain—or for all temperatures.

Sandford and I* have investigated the effect of grain size more thoroughly with tin and some tin alloys. Tests were carried out at room temperature, which is above the temperature of recrystallization of these alloys. The material used was always annealed in the ingot form to produce constitutional equilibrium and then worked and heat-treated to give a wide range of grain sizes. Creep tests at a constant load were carried out and the duration before fracture and the minimum creep rate were found. Typical results for tin are shown in Fig. 38. Grain sizes are recorded as the number of grains in the cross section, as this is more fundamental than the actual grain size. The results show that the duration reaches a maximum with a grain size of 300 in the cross section, while the minimum creep-rate curve shows a minimum at the same point. This is a logical result, as, if the coarser grain size had a better creep resistance over the whole range of grain size, a single crystal would be the strongest form under creep. The existence of an optimum grain size in some tin alloys has also been confirmed but the generality of the observations has not been established.

No convincing explanation of the effect of grain size has yet been offered. It is, however, clear that a large grain size is inherently more stable than a fine grain. It is also true that the processes by means of which large crystals are commonly produced, which involve longer times of heating or higher temperatures, may produce more stable internal structures. If the temperature is such that grain growth may occur, even very slowly, the metal will be liable to flow the more readily the finer the grain. Moreover, although fine grains are more resistant to slip with rapid rates of strain by reason of the interference of the crystals

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* Unpublished data.

with one another, it is by no means inconceivable that they would prove to be less resistant to thermal flow at low rates of strain owing to the same cause. Moreover, the disturbance caused by deformation of a fine-grained metal, being more profound, might be expected to oppose further slip, but to facilitate thermal flow. Thus the differences might be accounted for by a change in the mechanism of flow. The maximum that occurs at a comparatively large crystal size might be accounted for by a scale effect as the crystal size approached that at which the influence of the individual crystals is felt. The statistical average effect of a multicrystalline mass must at some stage be influenced, as the grain size increases, by the directional properties of individual crystals.

Note

Since the above lecture was written, papers by Moore, Betty and Dollins (Univ. Illinois *Bull.* (1938) **35,** 102) and by Greenwood and Worner (*Jnl.* Inst. Metals, Feb. 1939) have come to the writer's notice. They deal with some of the matters referred to in the lecture, but it has not been possible to include any account of them in the lecture.

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An X-ray Study of the Iron-palladium and Nickel-palladium Systems

By Ralph Hultgren,* Member, and Carl A. Zapffe,† Junior Member A.I.M.E.

(New York Meeting, February, 1939)

Few phase diagrams of alloys composed of two transition metals have been adequately studied, probably because of the high melting points involved. Transition metals are the elements that have inner shells incompletely filled with electrons. They comprise groups III*a* to VIII*a* of the periodic table, including more than half of all metals.

We have chosen to study two systems whose comparatively low melting points allowed the alloys to be melted in a molybdenum resistance furnace. The nickel-palladium system proved to consist of a simple series of solid solutions, but iron-palladium manifested several remarkable features. The main characteristics of the latter diagram were decisively established, but lack of time prevented precise determination of phase boundaries. The gamma to alpha transformation in this system is unusual and warrants further study.

Grigorjew[1] determined the liquidus and solidus of the iron-palladium system by thermal methods. He found a minimum melting point, but no eutectic. He also found that palladium lowered the gamma to alpha and raised the gamma to delta transformation temperatures of iron, with a complete series of solid solutions existing between gamma iron and palladium. His measurements also indicated a compound or superlattice near the composition $FePd_3$.

Jellinghaus[2] found that annealing at 500° C. greatly increased the magnetic coercive force of an alloy of composition FePd. X-ray diffraction photographs showed that a tetragonal ordered phase had formed during the anneal.

Hocart and Fallot[3,17] made magnetic measurements over the entire range of composition. They found that less than 5 atomic per cent Pd

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* Assistant Professor of Metallurgy, Graduate School of Engineering, Harvard University, Cambridge, Mass.

† Research Associate, Battelle Memorial Institute, Columbus, Ohio.

[1] References are at the end of the paper.

was soluble in alpha iron, in contrast to the other platinum metals, which are quite soluble. Between 5 and 40 atomic per cent, two Curie points were found, one at 764° C. and one at 432° C. This is characteristic of two-phase regions. For higher percentages of palladium, the Curie point depended on the heat-treatment. In alloys quenched from 1150° C., it decreased regularly with increasing palladium content. In the same alloys cooled slowly for 100 hr. between 800° C. and 400° C., the Curie points reached a maximum at 48 and at 74 atomic per cent Pd. X-ray photographs showed that a second phase was beginning to form, but most of the alloy was still in the disordered face-centered-cubic form stable at high temperatures. No satisfactory structure determinations of the new phases were possible.

The present writers[4] were able by more thorough annealing to complete the transformations, and found that in both cases superlattices had formed, which were isomorphous with AuCu and $AuCu_3$, respectively. The structure determination of Jellinghaus[2] was corrected.

The liquidus and solidus of the nickel-palladium system have been determined by Heinrich[5] and by Fraenkel and Stern.[6] Their determinations agree fairly closely and show a minimum melting point at 45 atomic per cent Pd. A complete series of solid solutions is indicated. Fraenkel and Stern found some evidence of a miscibility gap at lower temperatures, but the work of Heinrich[5] and of Grigorjew[7] contradicts this.

Methods and Materials

Sponge palladium with a stated purity of 99.8 per cent was purchased from the American Platinum Works, Newark, N. J. The lattice constant was found to be 3.8827 Å., compared with 3.8823 Å. given by Wyckoff[8] for pure palladium.

The International Nickel Co. kindly furnished high-purity nickel powder.* The lattice constant was found to be 3.5168 Å., agreeing exactly with the value of Jette and Foote[9] for pure nickel. After treatment with hydrogen at a red heat, it was stored in a desiccator preparatory to use.

High-purity carbonyl iron, furnished by the Naval Research Laboratories at Washington, D. C., was used. It contained carbon 0.0022 per cent, and silicon 0.0012 per cent, according to the analysis given. The lattice constant was 2.8607 Å., compared with 2.8605 Å. given by Jette

* Commercially pure nickel shot was examined and found to be inhomogeneous. Although the analysis given indicated 99.88 per cent purity, lattice constants varied from one shot to another and from inside to outside of the same shot. The range of values was 3.5173 to 3.5200 Å.

and Foote[9] for pure iron. It was filed to powder form with negligible contamination from the file.

Weighed quantities of the metal powders were mixed and melted in a vacuum in crucibles of pure aluminum oxide. These crucibles, 1 cm. in diameter and 2 cm. tall, were made by the Lava Crucible Co. of Pittsburgh. The company reported that they contained "98 per cent Al_2O_3 with TiO_2 the largest impurity with a very small amount of Fe_2O_3 and SiO_2." No binder had been used. The melting was done in a molybdenum-wound resistance furnace insulated with silica brick. Furnace and insulation were encased in a water-cooled copper shell, which was evacuated by a mercury diffusion pump backed by a Hyvac. A cold trap was placed between furnace and diffusion pump. A window of Pyrex glass allowed melting to be observed. The ingots obtained were cold-worked by hammering and sealed off in evacuated Vitreosil tubes. The samples were then given a long homogenizing anneal.

Considerable difficulty was at first experienced in attaining homogeneity. Months of anneal at 1000° C. was not sufficient. Microscopic examination showed that some grains had not fused together, either because of incomplete melting or oxide coatings. A more drastic treatment was adopted.

The powders were briquetted in a steel mold before melting, to insure intimacy of contact. When the furnace had attained a red heat, hydrogen was admitted and pumped out several times in order to reduce oxides. A crucible containing pure palladium (melting point 1555° C.) was placed on top of the others and the temperature of the furnace was increased until the palladium was observed to melt. The high temperature was maintained for about 10 min. before the power was shut off. This insured that the alloys were several hundred degrees above their melting points for some time. The temperature of the homogenizing anneal was also increased. It was found by trial that Vitreosil tubes would retain a vacuum for several days at 1300° C. before devitrification became serious. Since the melting points of most of the alloys were below 1400° C., homogenizing near the melting point was possible. Anneals of two days at 1300° C. or five days at 1200° C. were carried out, then the sample was cold-worked and the anneal repeated as often as necessary. Caution was necessary to prevent cracking during cold-work. Between anneals samples were cleaned by filing. This technique succeeded in obtaining homogeneity, as evidenced by sharp back-reflection X-ray lines obtained from mixtures of powders filed from several places on the ingot. Each homogeneous ingot was chemically analyzed for both constituents.

Final anneals were performed on powder samples filed from these ingots. The powders were sealed in evacuated Pyrex or Vitreosil tubes, which were lowered into furnaces maintained at constant temperatures

by pyrometer controllers. Precautions* were taken to minimize temperature gradient, and it is estimated that temperatures remained constant within 3° C. Upon completion of the anneal, the samples were expelled with a steel rod and broken on an anvil under water or alcohol. The latter was necessary to avoid corrosion in the iron-palladium system. By this means, a very rapid quench was obtained. Times of anneal varied from four days at 800° C. to three weeks at 400° C.

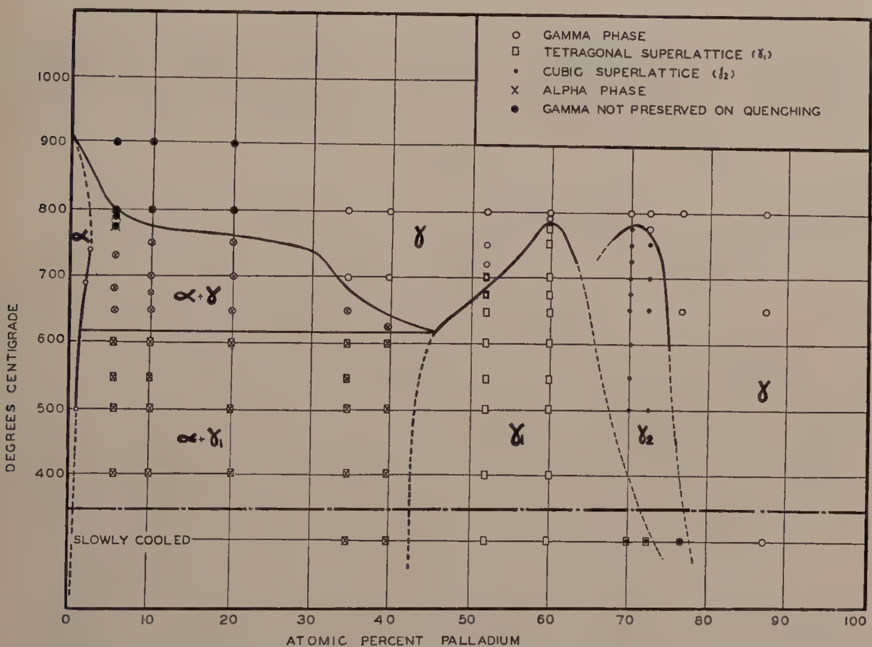

FIG. 1.—THE IRON-PALLADIUM SYSTEM.

The quenched powders were studied by X-ray diffraction methods. The phases present were identified from Debye photographs, while precision lattice constants were determined with the aid of a back-reflection focusing camera,[9] using Cohen's method of calculation.[10]

IRON-PALLADIUM SYSTEM

Confirming the magnetic results of Hocart and Fallot,[3] it was found that palladium has little solubility in alpha iron and that at lower temperatures there is a two-phase region up to more than 40 atomic per cent Pd. At elevated temperatures, gamma iron and palladium seem to be completely miscible, although in high-iron samples the gamma phase

* For a more complete description of the annealing and quenching technique used, see A. S. Coffinberry and R. Hultgren: *Trans.* A.I.M.E. (1938) **128**, 249.

cannot be preserved by quenching. The gamma phase forms two superlattices[4] to which we will assign the formulas FePd and $FePd_3$. The first is tetragonal, isomorphous with AuCu, and the second cubic, like $AuCu_3$. Fig. 1 shows the phases present at each temperature and

FIG. 2.—DEBYE PATTERNS OF IRON-PALLADIUM SAMPLE CONTAINING 10 ATOMIC PER CENT PALLADIUM.
Quenched from 675° C. (above) and 800° C. (below).

composition investigated. The phase boundaries drawn in Fig. 1 are not to be regarded as exact.

GAMMA TO ALPHA TRANSFORMATION

Debye patterns of alloys containing 5.5, 10, and 20 atomic per cent Pd showed a well defined two-phase region at temperatures below 750° C. The lines of both phases were sharp.

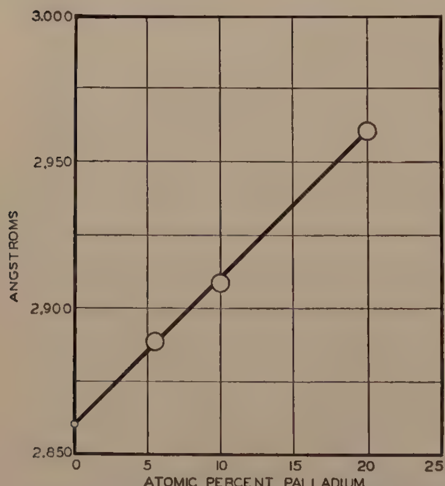

FIG. 3.—LATTICE CONSTANTS OF BODY-CENTERED CUBIC PHASE PRODUCED BY QUENCHING FROM GAMMA RANGE.

The same samples quenched from 800° C. gave quite different results. Diffraction lines of a single body-centered cubic lattice appeared in the Debye patterns (Fig. 2). The lines were diffuse, the diffuseness increasing with the amount of palladium in the sample. As shown in Fig. 3, the lattice constants of this phase increased practically linearly with palladium content, indicating that the palladium was dissolved. The expansion of the lattice is about twice as great as predicted by Vegard's law. This is consistent with the large positive deviation found in the gamma phase.

A large increase in solubility at this temperature seems improbable and is inconsistent with the stabilization of gamma by palladium. Moreover, much the same patterns were obtained from samples quenched from

900° C., a temperature only slightly below the gamma to alpha transformation of pure iron. It seems almost certain that the samples have been quenched from the gamma range with the gamma phase transforming during the quench. The diffuseness of the diffraction lines suggests lack of equilibrium, which is in accord with this explanation.

Fallot's[17] magnetic determinations of the temperatures of decomposition of gamma substantiate this interpretation. His results are not precise because of a large hysteresis, but in all cases the curve of Fig. 1 lies between his lower and upper limits.

Thus, it appears that during the quench there has been a mass transformation of structure from face-centered to body-centered cubic, in which palladium is held in supersaturated solid solution.

In quenches from the two-phase region, the gamma phase contained more than 20 atomic per cent Pd and was preserved, except for the two cases noted below. The positions of the gamma lines depended only on the annealing temperature and not on composition, which is characteristic of equilibrium in a two-phase region. For annealing temperatures of 600° C. and below, certain lines of the gamma phase were split, showing the tetragonal symmetry of the FePd superlattice.

Debye patterns of the 5 per cent Pd sample quenched from 775° and 790° C. showed no gamma phase and two body-centered cubic patterns. One of these, with sharp lines, had the lattice constant to be expected of a saturated alpha phase. The other, with diffuse lines, had considerably larger lattice constants, which, calculating from Fig. 3, indicated the presence of about 10 atomic per cent Pd at 775° C. and 7.5 atomic per cent at 790° C.

Alpha Phase

The lattice constants of alpha in equilibrium with gamma were only slightly larger than those of pure iron. Since no samples within the alpha range of homogeneity were examined, the lattice constant-composition curve could not be drawn. If Fig. 3 is assumed to represent

Table 1.—*Solubility of Palladium in Alpha Iron*

Temperature of Anneal, Deg. C.	Lattice Parameter of Alpha Phase	Estimated Solubility of Palladium	
		Atomic Per Cent	Weight Per Cent
Pure iron	2.8607[a]		
740	2.8728	2.4	4.5
690	2.8695	1.8	3.4
500	2.8651	0.9	1.7

[a] Pure iron.

this curve, the solubilities of palladium in alpha iron can be calculated (Table 1).

TABLE 2.—*Lattice Constants of Gamma Phase of Iron-palladium System*

Atomic Per Cent Palladium	Lattice Constant (25° C.)	Atomic Per Cent Palladium	Lattice Constant (25° C.)
0	(3.564)[a]	70.2	3.8367
34.4	3.7568	72.4	3.8420
39.5	3.7746	76.6	3.8496
51.9	3.8015	87.3	3.8626
59.8	3.8177	100.0	3.8827

[a] Value quoted by Neuburger.[16]

GAMMA PHASE

The lattice constants of the gamma phase are tabulated in Table 2. Cobalt-manganese radiation was used to determine them. As shown in Fig. 4, there is a strong positive deviation from Vegard's law.

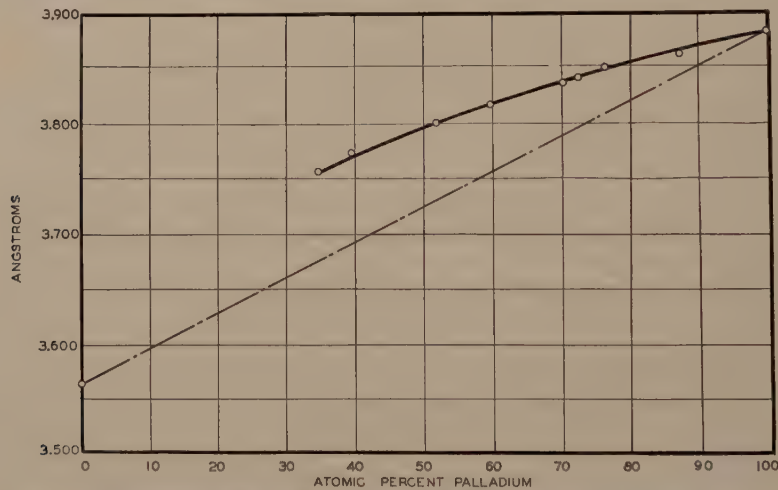

FIG. 4.—LATTICE CONSTANTS OF GAMMA PHASE OF IRON-PALLADIUM SYSTEM. Lattice constant of gamma iron taken from Neuburger.[16]

TETRAGONAL FePd SUPERLATTICE

At intermediate compositions, the gamma phase became ordered on slow cooling, forming a tetragonal superlattice[4] with c/a less than 1, in disagreement with the determination of Jellinghaus,[2] who found $c/a > 1$. Iron and palladium atoms occupy alternate layers parallel to (001). The structure is isomorphous with AuCu.

A sample containing 51.9 atomic per cent Pd quenched from 650° C. gave the following lattice constants:

$$a_0 = 3.852 \qquad c_0 = 3.723 \qquad c_0/a_0 = 0.9664$$

At lower temperatures c/a decreased, and, surprisingly, it decreased at higher palladium contents. The volume of this unit cell is 55.24 Å.,^{3} compared with 54.94 Å.^{3} for the disordered gamma phase, an increase of 0.5 per cent on ordering.

Although in an AuCu type of superlattice, the critical temperature of ordering normally has a maximum at 50 atomic per cent, the only composition at which perfect order is possible, this was not true for FePd. The critical temperature for the 51.9 atomic per cent alloy was near 700° C., but order persisted up to 775° C. with 60 atomic per cent Pd.

In the former alloy, the ordered and disordered phases were found together in samples quenched from 675° and 700° C. A number of other investigators have reported ordered and disordered phases present simultaneously. Since all the work had been done with short anneals, it has not been considered proved that the two phases were in equilibrium. Bragg and Williams[11] regard ordering as a continuous process without taking account of the possibility of an intermediate two-phase region. Nix and Shockley[12] consider such regions theoretically inevitable but perhaps not realizable experimentally.

The equilibrium was approached from above and below the ordering temperatures in an attempt to decide whether the ordered and disordered phases were in equilibrium with one another. A portion of the 51.9 per cent Pd powder was annealed for a week at 600° C., at the end of which time an X-ray diffraction photograph showed it to be completely ordered. Two other portions of the same sample were annealed for two days at 750° C. One of them was quenched and found to be completely disordered. The other remained in the furnace while it was cooled to 690° C. At this point, the ordered sample was inserted and both were annealed for 15 days at this temperature before quenching. The ordered sample had become partly disordered, but the disordered sample was unchanged. While this does not demonstrate the absence of a two-phase equilibrium, it does show that the transformation is very sluggish and renders it probable that disorder is the equilibrium phase at this temperature. As Barrett[13] has pointed out, it is impossible to demonstrate experimentally the absence of a two-phase region between order and disorder. Slow rates of transformation could account for all the existing evidence of a two-phase region.

The $FePd_3$ Superlattice

At higher palladium contents, there was found another ordered state with cubic symmetry,[4] which is isomorphous with $AuCu_3$. Just as with FePd, it was not most stable at its theoretical composition.

Some samples in the cubic superlattice region had partly transformed to tetragonal when they were slowly cooled from 600° C. to room tem-

perature over a period of 15 days. Similarly, the 76.6 atomic per cent Pd sample was found to be partially ordered with the slowly cooled anneal.

In this superlattice also there was an increase in atomic volume on ordering, amounting to about 0.3 per cent.

Nickel-palladium System

All the nickel-palladium alloys studied were face-centered cubic under all annealing conditions. No compounds, superlattices, or miscibility gaps were detected in annealing periods as long as two weeks at 600° C. and three weeks at 400° C. as well as slow cooling from 600° C. over a period of 15 days. It was concluded that the miscibility gap reported by Fraenkel and Stern[6] was absent.

The lattice constants of the nickel-palladium alloys are given in Table 3. Fig. 5 shows that they follow a smooth curve with a considerable positive deviation from Vegard's law.

Table 3.—*Lattice Constants of Nickel-palladium System*

Atomic Per Cent Palladium	Lattice Constant (25° C.)	Atomic Per Cent Palladium	Lattice Constant (25° C.)
0	3.5168	49.7	3.7302
11.2	3.5699	60.1	3.7667
11.7	3.5750	64.2	3.7806
15.7	3.5897	64.3	3.7796
25.3	3.6345	77.9	3.8296
34.5	3.6779	86.0	3.8859
40.0	3.6920	100.0	3.8827
47.8	3.7274		

Discussion of Results

In both systems, there is a positive deviation from Vegard's law of additivity of atomic radii. Neither system forms any compounds, in agreement with a generalization made by Jette[14] that compound formation is always accompanied by negative deviation from Vegard's law in the terminal solid solutions.

Three peculiarities of the iron-palladium system are worthy of note; namely, the gamma to alpha transformation, the increase of atomic volume on ordering, and the displacement of the most stable composition of the superlattices from the theoretical value.

Gamma iron containing moderately small amounts of palladium in solid solution decomposes below the critical temperature into alpha iron that is almost pure and a gamma phase richer in palladium. If the gamma-iron solid solution is quenched, however, the decomposition is arrested at an intermediate stage. Under the quenching conditions, the

face-centered cubic lattice transforms en masse into a body-centered cubic one. Diffusion necessary for precipitation is suppressed. The palladium atoms, trapped by lack of mobility, are carried into the body-centered lattice. Apparently no similar gamma to alpha transformation has been reported in the literature except in martensite.*

Martensite, which is produced on quenching under suitable conditions, is considered to be an intermediate stage in the decomposition of austenite into alpha iron plus cementite. It is body-centered and contains much more dissolved carbon than the alpha phase. The dissolved carbon distorts the cubic symmetry into a tetragonal one, the distortion being proportional to carbon content. Martensite thus resembles an alpha phase containing excess carbon in a supersaturated solution.

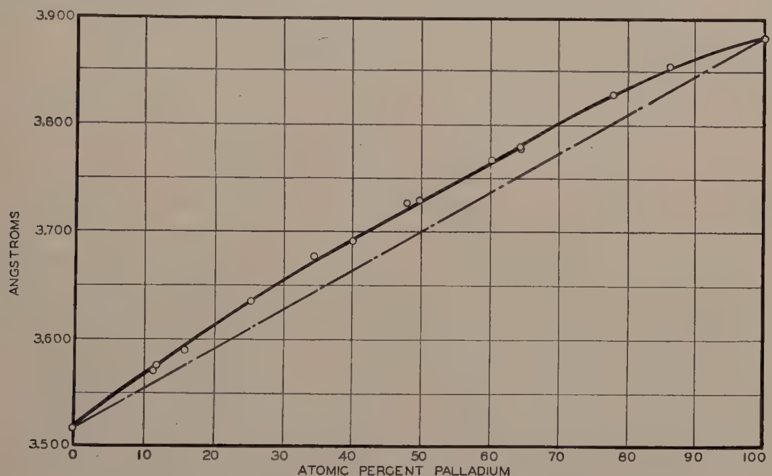

FIG. 5.—LATTICE CONSTANTS OF NICKEL-PALLADIUM SYSTEM.

The similarities are obvious, but several differences should be noted. First, palladium is dissolved in a substitutional solid solution while carbon is in an interstitial one. Second, the palladium sample transforms homogeneously into one phase in the samples studied, while austenite is observed to accompany martensite in high-carbon samples. Third, the palladium phase is cubic while martensite is tetragonal.

The palladium phase is easier to prepare than martensite and the transformation should be easier to study. Probably further work on this transformation would yield valuable results in the study of the decomposition of gamma phases.

The increase of atomic volume on ordering is anomalous. As a general rule, the atomic volume decreases and we know of no other case of an increase. We suggest that this might be due to ferromagnetism.

* We have been greatly assisted in our discussion of the martensite transformation by conferences with Prof. A. B. Greninger and Mr. A. R. Troiano, of this laboratory.

It has already been mentioned that Hocart and Fallot[3] and Jellinghaus[2] found that ordering profoundly influenced magnetic properties, although they did not give magnetic saturation values.

Köster and Schmidt[15] have deduced from thermal expansion measurements that ferromagnetism increases the atomic volume of iron 1.6 per cent at room temperature, of cobalt 2.3 per cent, and of nickel 1.0 per cent. Hence, if the superlattices were more ferromagnetic than the disordered state, the expansions of 0.5 per cent for FePd and 0.3 per cent for $FePd_3$ could be easily accounted for.

Summary

Nickel and palladium form a complete series of solid solutions in which no compounds, superlattices or miscibility gaps were detected. There is a positive deviation from Vegard's law.

Palladium is only slightly soluble in alpha iron but forms a complete series of solid solutions with gamma iron, with a large positive deviation from Vegard's law. An intermediate stage in the decomposition of gamma iron containing dissolved palladium was found and compared with the martensite transformation. Two superlattices were found, FePd and $FePd_3$. FePd is tetragonal, isomorphous with AuCu and $FePd_3$ is cubic, isomorphous with $AuCu_3$. Neither is most stable at its theoretical composition. There is an anomalous increase of atomic volume on ordering, which possibly is due to ferromagnetism.

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Equilibrium Relations in Aluminum-zirconium Alloys of High Purity

BY WILLIAM L. FINK,* MEMBER A.I.M.E. AND L. A. WILLEY*

(Detroit Meeting, October, 1938)

Two of the aluminum-alloy systems previously studied—the aluminum-titanium and the aluminum-chromium—exhibit a peritectic reaction at the extreme aluminum end of the diagram. Preliminary work indicated that the aluminum-zirconium and certain other aluminum systems were similar in this respect. The present paper, the twentieth of a series from the Aluminum Research Laboratories, reports the results of a recent investigation of equilibrium relations in aluminum-zirconium alloys of high purity, which confirm the preliminary observations.

PREVIOUS INVESTIGATIONS

There has been only one investigation of the aluminum end of the aluminum-zirconium system. Sykes[1] prepared and studied alloys containing 0 to 70 per cent Zr. The lowering of the freezing point of aluminum by the addition of zirconium was found to be very little, if any (less than 2° C.). He placed the solid solubility of zirconium in aluminum at room temperature between 0.57 and 0.97 per cent.

A few other investigators have attempted to determine the composition of the intermetallic compounds occurring in this system. Hönigschmid[2] obtained the compound $ZrAl_3$ as a by-product during the preparation of $ZrSi_2$. He made no attempt to prepare other aluminum-zirconium compounds. Weiss and Newmann[3] prepared an alloy by heating aluminum with a double fluoride of potassium and zirconium. When this alloy was treated consecutively with caustic soda and hydrochloric acid, there was a residue, which contained approximately 72 per cent Zr and 28 per cent Al (Zr_3Al_4). Marden and Rich[4] prepared an alloy in the same way, treated it with caustic soda, and obtained a residue of silver-white crystals, which contained 70 per cent Zr and 30 per cent Al (Zr_3Al_4).

ALLOYS

Materials Used.—Electrolytically refined aluminum was employed for the preparation of all alloys used in this investigation. The chemical

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* Aluminum Research Laboratories, New Kensington, Pa.

[1] References are at the end of the paper.

analyses showed the following impurities: 0.004 per cent Si, 0.003 to 0.004 per cent Fe and 0.004 to 0.005 per cent Cu.

The alloys were prepared from metallic zirconium (total zirconium = 95.7 per cent) obtained from the Titanium Alloy Manufacturing Co. The chief impurity in this material was zirconium oxide, which was, of course, innocuous in the present investigation. The other impurities were: Si, 0.12 per cent; Fe, 0.36; Ti, 0.03; C, 0.98. Spectrographic analysis revealed magnesium, copper, calcium, barium, chromium, manganese, vanadium, nickel and aluminum in such small amounts that they could not be determined by ordinary chemical methods.

Preparation of Alloys.—An alloy containing about 4 per cent Zr was first prepared by adding the metallic zirconium in lump form to the high-purity aluminum in a No. 3 alundum-lined plumbago crucible at temperature between 1100° and 1200° C. An electrolytically purified fluoride flux was used to retard oxidation and to aid in wetting the zirconium with aluminum.

TABLE 1.—*Chemical Analysis of Alloys*

Alloy No.	Weight Percentage				Remarks
	Si	Fe	Cu	Zr	
S-29292	0.020	0.007	0.005	4.04	
S-29395	0.06	0.01	0.01	3.02	
S-31335	0.004	0.003	0.004		Alloys for solid solubility determinations (made from hardener S-29292)
S-31336	0.004	0.004	0.005	0.02	
S-31337				0.04	
S-31338				0.10	
S-31339				0.13	
S-31340				0.19	
S-31341				0.28	
S-31342				0.37	
S-31343				0.47	
S-31344				0.55	
S-31345				0.69	
S-31346	0.007	0.005	0.004	0.87	
S-32582	0.007	0.003	0.005	0.44	Alloys for thermal analysis
S-30299				0.71	
S-32609	0.050	0.006	0.006	2.06	

Alloys for the determination of solid solubility were prepared by the addition of the required amount of the 4 per cent Zr alloy to high-purity aluminum at 950° to 1000° C. Two of the alloys for thermal analysis were prepared in the same way but from another aluminum-zirconium alloy containing approximately 3 per cent Zr. The alloys for the solid solubility determination were cast in a cold iron mold in the form of ingots

20 by 50 by 88 mm. The samples for analysis were also cast in cold iron molds in the form of slabs 4 by 40 by 75 mm.

Chemical Analysis.—All of the alloys were analyzed for zirconium by the pyrophosphate method.[5] The results are given in Table 1.

Thermal Analysis

The thermal analyses were made on 200-gram samples, which were prepared and heated to 1000° C. in a straight-walled graphite crucible (40 mm. inside dia. by 100 mm. deep), which was provided with a graphite cover. Since the primary thermal arrest in hyperperitectic alloys of this type are weak and usually depressed because of undercooling, no attempt was made to investigate the liquidus curve by thermal analysis; therefore the sample was rapidly cooled from 1000° C. to about 700° C. At this point, the thermocouple was introduced and the cooling continued at the rate of from 2° to 5° C. per minute.

The 22-gauge chromel-alumel thermocouple was protected from the melt by a Pyrex glass tube coated with a thin layer of alundum cement and lampblack. The outside diameter of the coated tube was 4 mm. The potential of the couple was read with a Leeds and Northrup type K potentiometer. The couple was calibrated against the freezing point of electrolytically refined aluminum (660.2° C.)* immediately before and after the thermal analysis of each alloy. The average of the calibration before and after an analysis was taken as equivalent to the freezing point of high-purity aluminum. For the cooling curves, the couple was calibrated by running cooling curves, and for the heating curves the couple was calibrated by running heating curves. On both cooling curves and heating curves, the peritectic temperature was 660.5° C.

Determination of Liquidus

The determination of the liquidus or, in other words, the solubility curve of zirconium in molten aluminum, was made by a method similar to that used in determining these curves in systems previously investigated.[6] Three kilograms of the hardener containing approximately 3 per cent Zr was heated to about 975° C. in a No. 10 alundum-lined plumbago crucible in a small electric crucible furnace. The temperature was held constant within ±3° C. by means of a Wilson-Maeulen controller. A protected thermocouple was placed just below the surface of the metal and was connected to a Brown portable potentiometer for the determination of the temperature near the surface of the metal. When the metal was up to temperature, it was stirred vigorously for several

* In previous papers this grade of aluminum was considered to melt at 660.0° C. Later work by the National Bureau of Standards and the Aluminum Research Laboratories has given 660.2° C. as the melting point. A correction of 0.2° C. should therefore be made in previous results.

minutes to insure saturation of the aluminum with zirconium. The alloy was then permitted to stand undisturbed for ½ hr. at constant temperature. During this time, the undissolved crystals of α(Al-Zr) settled to the bottom of the crucible because they were more dense than the melt. The dross was then carefully removed from the center of the surface and a small preheated ladle was filled with clean surface liquid. This liquid was cast immediately into the form of a slab 4 by 40 by 75 mm., to be used for chemical analysis. The heating was continued at this same temperature for an additional 15 min. When a second sample of the liquid was taken in the same way, the temperature of the furnace was decreased about 25° C. and two samples were taken in the same manner

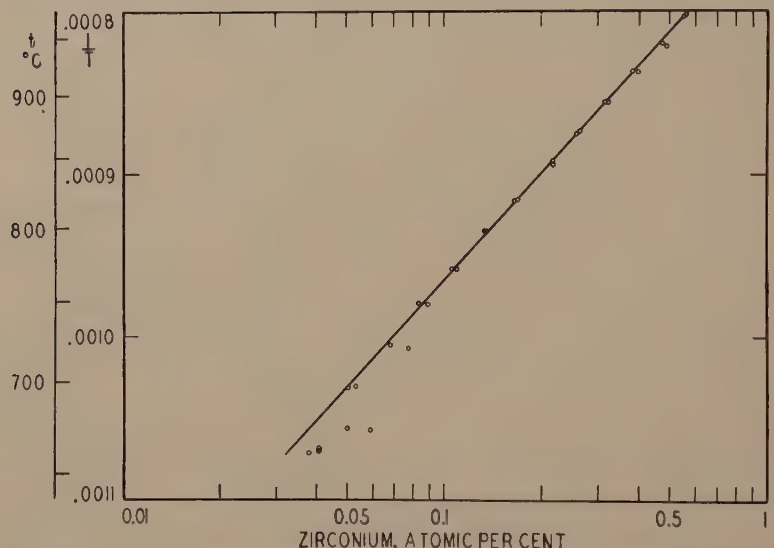

FIG. 1.—SOLUBILITY OF ZIRCONIUM IN LIQUID ALUMINUM.

as at the higher temperature. This procedure was repeated approximately every 25° C. until the temperature of 673° was reached. Two samples were taken in a similar manner at 662° C. A final sample was taken from the center surface of the solidified ingot. The results of this determination are given in Table 2 and Fig. 1.

As shown in Fig. 1, all of the samples above 673° C. fall along a straight line when plotted as the logarithm of atomic per cent of zirconium against the reciprocal of the absolute temperature. The points at 673° C., and perhaps those at lower temperatures, are off the line by an amount exceeding the analytical error. Either equilibrium had not been attained or crystals of the solid phase were unintentionally included. The sample taken from the solidified ingot gave results closer to the line than might have been expected.

TABLE 2.—*Solubility of Zirconium in Liquid Aluminum*

First Sample			Second Sample		
Sample No.	Temperature of Equilibrium, Deg. C.	Zirconium, Per Cent	Sample No.	Temperature of Equilibrium, Deg. C.	Zirconium, Per Cent
S-29395-1	974	1.89	S-29395-2	972	1.86
S-29395-3	944	1.64	S-29395-4	946	1.59
S-29395-5	921	1.34	S-29395-6	921	1.29
S-29395-7	895	1.08	S-29395-8	895	1.06
S-29395-9	871	0.89	S-29395-10	870	0.87
S-29395-11	846	0.73	S-29395-12	848	0.73
S-29395-13	819	0.57	S-29395-14	819	0.56
S-29395-15	796	0.46	S-29395-16	796	0.45
S-29395-17	771	0.37	S-29395-18	771	0.36
S-29395-19	747	0.30	S-29395-20	748	0.28
S-29395-21	720	0.26	S-29395-22	722	0.23
S-29395-23	697	0.17	S-29395-24	698	0.18
S-29395-25	673	0.20	S-29395-26	674	0.17
S-29395-27	662	0.14	S-29395-28	663	0.14
S-29395-29	660.5	0.13	Sample from surface of solidified ingot		

SOLID SOLUBILITY

The solid solubility was determined by both electrical resistivity measurements and metallographic examination.

The ingots previously described were given a homogenizing treatment at 630° C. for 100 hr. and were quenched in cold water. They were then cold-rolled from 20.0 mm. to 6.5 mm. in thickness. The slabs were heat-treated for 136 hr. at 475° C., to obtain a finely divided precipitate. They were then cooled in air at room temperature and cold-rolled to sheet 1 mm. thick. Specimens 13 mm. wide and approximately 500 mm. long were cut from the sheet for the electrical resistivity measurements. Specimens 20 by 25 mm. were cut from the sheet for microscopic examination.

The heat-treatment of all the specimens was carried out in an aluminum block (10 cm. inside dia., 20 cm. outside dia. and 53 cm. long) in a Leeds and Northrup homo furnace. The variation in temperature with respect to position in the block or with respect to time did not exceed $\pm 1°$ C. The heat-treatments of the specimen are listed in Table 3.

The electrical resistivity determinations were made by comparing the drop in potential across a known length of the specimen to that across a 0.001-ohm standard resistance while the same current was flowing through them in series. The potential measurements were made with a Leeds and Northrup type K potentiometer while the specimens were kept at a constant temperature of 25° C. in a thermostatically controlled oil

TABLE 3.—*Heat-treatments for Determination of (Al)-phase Limits*

Heat-treating Temperature, Deg. C.	Resistivity Specimens[a]		Metallographic Specimens[b]		
	Quenched in Cold Water and Resistivity Determined after Total Time at Temperature, Hr.		Time at Temperature, Hr.	Specimens Quenched in Cold Water	
	First Determination	Second Determination		Group No.	Marked
475	40	84	89		
500	70	116	118	1	500
550	45	67	69	2	550
600	45		45	3	600
640	21	43	21	4	640-1
640			45	5	640-45

[a] Only one set of resistivity specimens was used and the heat-treatments were carried out consecutively in the order given. Two to three hours time was required for the determination of resistivity. The specimens were withheld from the furnace for that length of time only.

[b] All five groups of metallographic specimens were placed in the furnace at the beginning and each group received all treatments previous to the time of quenching. The time required to change from one temperature to another was from two to three hours.

bath. The results of the electrical resistivity determinations after the final heat-treatment at each temperature, except at 475° C., are shown in Fig. 2. The treatment at 475° C. was merely for the purpose of obtaining the maximum number of small precipitate particles to facilitate the attainment of equilibrium at higher temperatures.

Equilibrium was closely approached at 500° C. and above except for three alloys just above the solid solubility limit at 500° and 550° C. The attainment of equilibrium was shown by constancy of resistivity with continued heating.

Another check on the attainment of equilibrium was obtained by plotting the solubility limit of zirconium as the logarithm of atomic per cent against the reciprocal of the absolute temperature as shown in Fig. 3. Plotted in this manner, the points fall on a straight line except that the point at 500° C. falls slightly off the line. It is probable that equilibrium was not quite attained at 500° C. and the solubility limit should be nearer 0.044 weight per cent than 0.050, as shown by the resistivity concentration curves.

The microscopic examination of the heat-treated and quenched specimens gave results in complete agreement with those obtained by electrical resistivity determination. The solid solubility limits determined by both methods are: 0.050, 0.084, 0.15, 0.23 per cent Zr by weight (0.015, 0.025, 0.045, 0.068 atomic per cent) at 500°, 550°, 600° and 640° C., respectively.

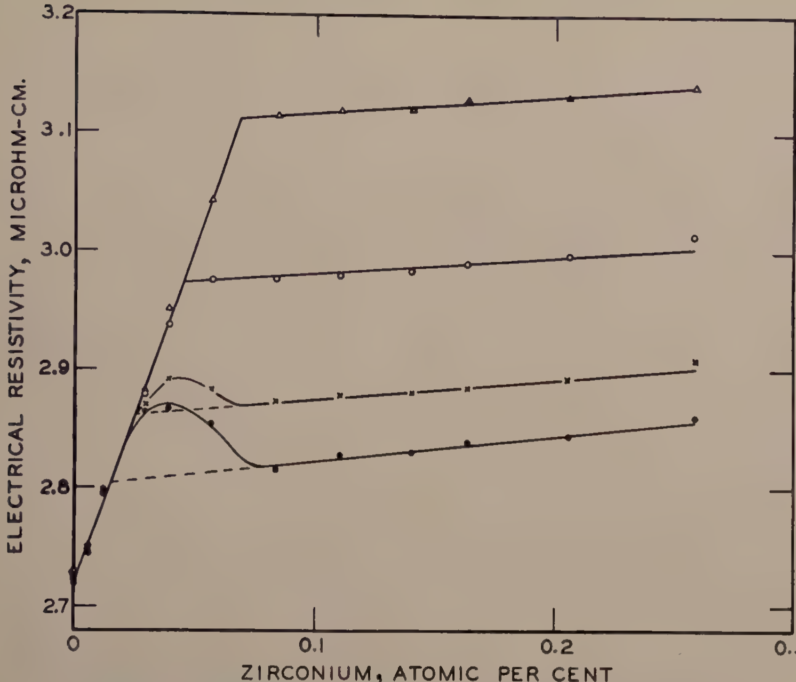

FIG. 2.—ELECTRICAL RESISTIVITY-CONCENTRATION CURVES.

● Electrical resistivity of alloys heat-treated at 500° C. and quenched.
× Electrical resistivity of alloys heat-treated at 550° C. and quenched.
○ Electrical resistivity of alloys heat-treated at 600° C. and quenched.
△ Electrical resistivity of alloys heat-treated at 640° C. and quenched.

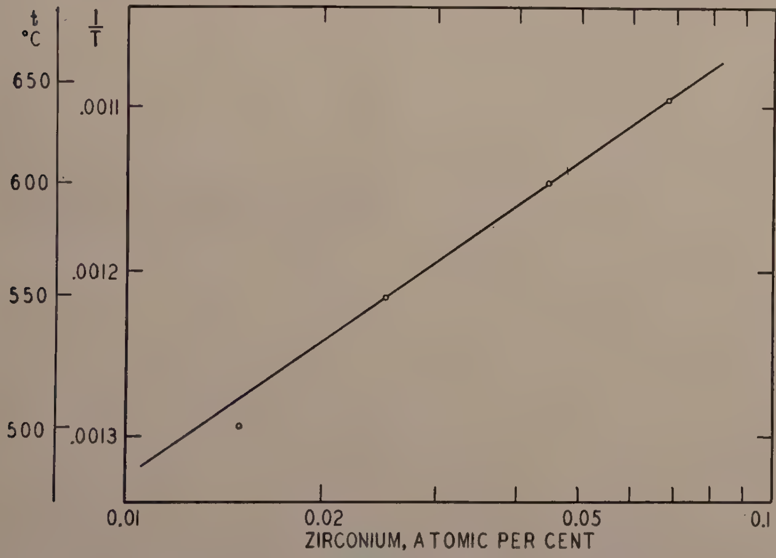

FIG. 3.—SOLUBILITY OF ZIRCONIUM IN SOLID ALUMINUM.

Structure of Aluminum-rich Aluminum-zirconium Alloys

Alloys containing 0.10, 0.13 and 0.19 per cent Zr showed precipitate particles of α(Al-Zr) both at the grain boundaries and within the grains after heat-treatment at 500° C. Fig. 4 shows the structure of an alloy

4 5

6 7

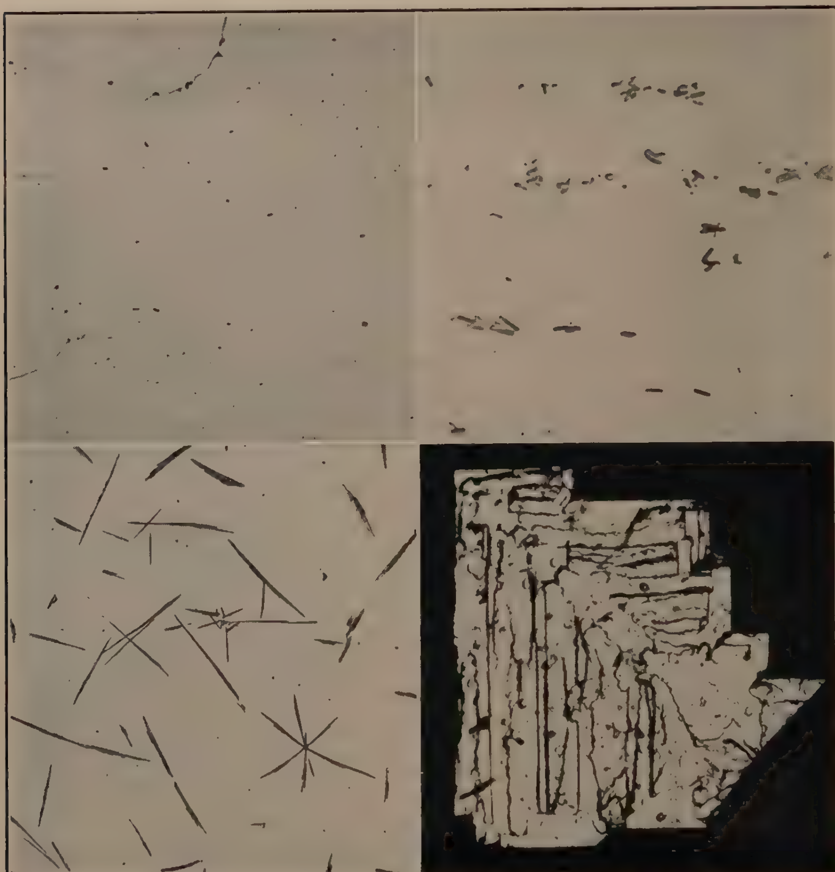

FIG. 4.—ALLOY CONTAINING 0.13 PER CENT ZR (S-31339-500—21248D). × 500.
Specimen heat-treated 89 hr. at 475° C., 118 hr. at 500° C. and quenched in cold water. Etched with 0.5 per cent HF.
Shows the α(Al-Zr) constituent precipitated from solid solution.

FIG. 5.—ALLOY CONTAINING 0.87 PER CENT ZR (S-31346-640-45—21249D). × 500.
Specimen heat-treated 89 hr. at 475° C., 118 hr. at 500° C., 69 hr. at 550° C., 45 hr. at 600° C., 45 hr. at 640° C. and quenched in cold water. Etched with 0.5 per cent HF.
Shows coalesced particles of the α(Al-Zr) constituent in the aluminum solid solution matrix.

FIG. 6.—ALLOY CONTAINING 2.06 PER CENT ZR (S-32609—21250D). × 100.
Specimen chill cast in a cold graphite mold.
Shows the primary α(Al-Zr) constituent in the chill-cast alloy.

FIG. 7.—PRIMARY CRYSTAL OF THE α(AL-ZR) CONSTITUENT (S-31745—20501D). × 15.
Specimen separated from aluminum solid solution with 10 per cent NaOH solution.
Shows form of the α(Al-Zr) constituent that occurs in aluminum-rich aluminum-zirconium alloys.

containing 0.13 per cent Zr after a final heat-treatment at 500° C. These heat-treated alloys containing 0.28 per cent or more of zirconium showed primary particles of α(Al-Zr). Fig. 5 shows the structure of an alloy containing 0.87 per cent Zr after a final heat-treatment at 640° C. The primary constituent has a needle-like appearance in a polished section of a cast alloy. Fig. 6 shows the structure of a chill-cast alloy containing 2.06 per cent Zr. Chemical separation of the constituent particles from the aluminum solid solution matrix (*vide infra*) revealed that they are very thin tabular crystals. A macrograph of one of these separated crystals is shown in Fig. 7.

Etching Characteristics.—The constituent appears light gray in the as-polished condition. None of the standard etching reagents[7] commonly used for the identification of constituents in aluminum alloys cause any alteration in the constituent. The constituent is, however, outlined

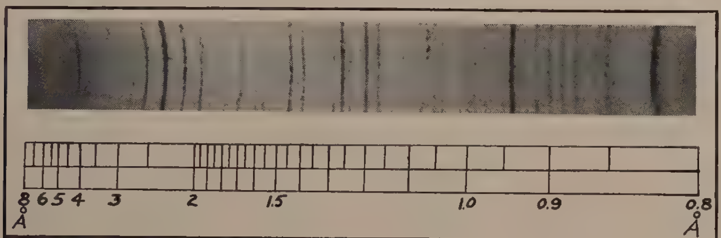

Fig. 8.—Debye-Scherrer pattern of α(Al-Zr).

when etched with solutions containing 0.5 per cent H_2F_2, 25 per cent HNO_3 at 70° C., 10 per cent NaOH at 70° C., and with a solution containing 0.5 per cent H_2F_2, 1.5 per cent HCl and 2.5 per cent HNO_3.

The Intermetallic Compound

Crystals of α(Al-Zr) were highly concentrated in the bottom section of the ingot that remained after the determination of the liquid solubility. A section from the bottom of this ingot was used for separation of these crystals. The sample was immersed in a 5 per cent NaOH solution, which dissolved the matrix but did not dissolve or attack the crystals of α(Al-Zr). Large, clean, well-developed crystals were selected under the microscope from the residue and analyzed for zirconium. The chemical analyses showed 52.5 and 53.3 per cent Zr by weight, which agrees closely with the zirconium content of Al_3Zr (53.0 per cent).

It is highly desirable to obtain a definite identification of the phases in alloy systems by preparing powder patterns. Fig. 8 shows the pattern of α(Al-Zr) taken with unfiltered CuK radiation. The particle size of the sample was so large that the lines are somewhat spotty. However, the pattern is adequate for identification of the compound.

As shown by the Laue pattern and its gnomonic projection, Fig. 9, the crystals of α(Al-Zr) are tetragonal, with an axial ratio of approximately 1.16 if the gnomonic net has been properly selected. No attempt has been made to determine the arrangement of atoms in the crystal.

Conclusions

The aluminum end of the aluminum-zirconium system has been investigated using high-purity alloys containing from 0 to approximately

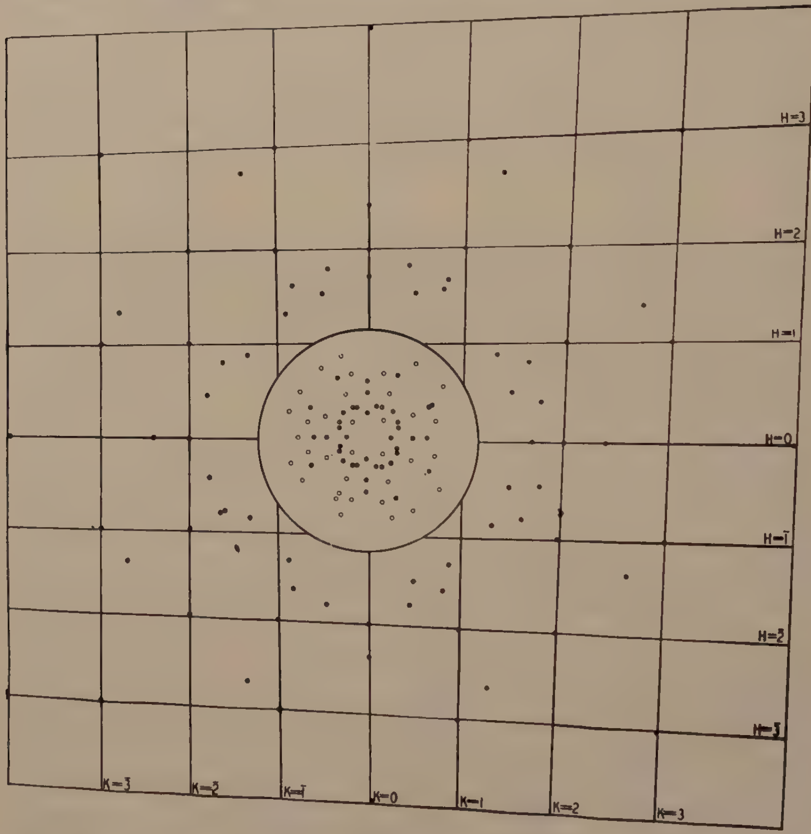

Fig. 9.—Laue pattern of primary crystal of α(Al-Zr) and its gnomonic projection.

2 per cent Zr. The equilibrium relations are summarized in the diagram of Fig. 10. A peritectic occurs at 660.5° C. between the melt containing 0.11 per cent Zr and α(Al-Zr) to form solid solution containing 0.28 per cent Zr. As the temperature decreases, the solid solubility decreases from 0.28 per cent Zr at the peritectic temperature to approximately 0.05 per cent at 500° C.

The zirconium-rich constituent α(Al-Zr) consists of very stable tabular tetragonal crystals, which are not discolored or attacked by

ordinary etching reagents. Chemical analysis has shown that α(Al-Zr) has a composition corresponding to the formula Al_3Zr.

ACKNOWLEDGMENT

The authors appreciate the valuable contributions of their colleagues to this investigation. They wish to mention specifically Mr. E. H. Dix, Jr., who initiated the program of which this paper is a part and has

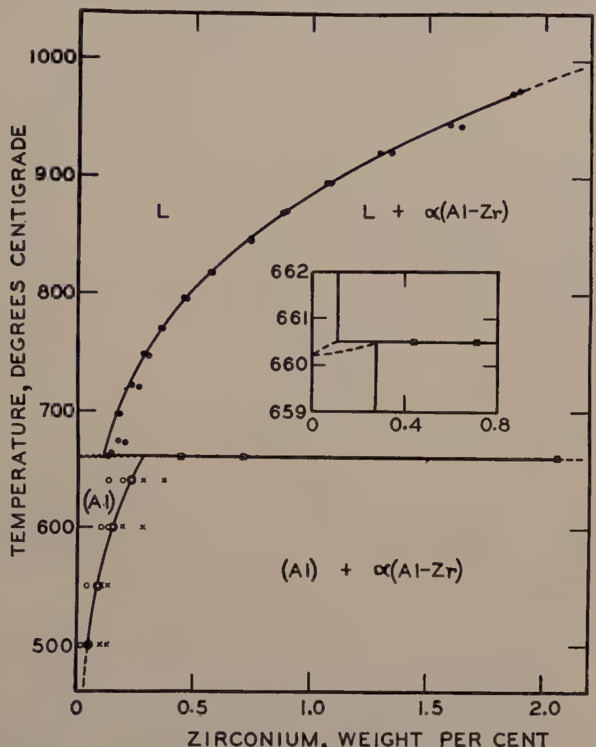

FIG. 10.—EQUILIBRIUM RELATIONS IN ALUMINUM END OF ALUMINUM-ZIRCONIUM SYSTEM.

- • From solubility determinations.
- ⊡ From thermal curves.
- ⊙ From electrical resistivity determinations.
- o From microscopic examination, aluminum solid solution.
- × From microscopic examination, aluminum solid solution + α(Al-Zr).

guided the course of the work; Mr. R. E. Schenck, who polished all of the microscopic samples and determined the etching characteristics, and Dr. H. R. Freche and Dr. D. W. Smith, who prepared the X-ray patterns and gnomonic projections.

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Solubility of Lead and Bismuth in Liquid Aluminum and Aluminum-copper Alloys

By L. W. Kempf* and K. R. Van Horn,* Members A.I.M.E.

(Detroit Meeting, October, 1938)

During the recent development of aluminum alloys for free-cutting screw-machine rod, it became desirable to know something of the solubility of lead and bismuth in liquid aluminum and in some aluminum alloys. The literature is not particularly helpful in supplying this information. These portions, therefore, of the constitutional relationships of aluminum-bismuth and aluminum-lead alloys were investigated by thermal analysis and by chemical analysis of samples taken from aluminum-rich melts in equilibrium with precipitated lead or bismuth. The solubility of lead and bismuth in some liquid aluminum-copper alloys was also investigated. Some consideration was also given to the solubility of these elements in solid aluminum.

Among the earliest investigators of the aluminum-lead and aluminum-bismuth systems was Wright,[1] who reported that melts of aluminum and lead formed two layers indicating limited liquid solubility. Under his conditions, the aluminum-rich layer was reported to contain 1.91 per cent Pb and the lead-rich layer, 0.07 per cent Al. Subsequently, Pecheau[2] found that in aluminum-rich alloy melts with more than 10 per cent Pb three layers were distinguishable. He reported that the middle layer contained from 3 to 10 per cent Pb. He also found that the melting point of aluminum appeared to be lowered slightly by the addition of lead. Gwyer[3] investigated these alloys and found evidence of a slight lowering of the freezing point of aluminum by the addition of either lead or bismuth. He found no evidence of solid solubility in either case and made no attempt to determine the liquidus curves. Hansen and Blumenthal[4] reported that the addition of lead distinctly lowered the solidification point of aluminum. They also found that bismuth lowered the melting point of aluminum. Guillet[5] reported almost complete mutual immiscibility for the aluminum-bismuth alloys in the liquid state. Bohner[6] examined the effect of various concentrations of lead and bismuth on the electrical conductivity of aluminum. He found decreases in conductivity on annealing at 500° C. as compared with the conductivity of the same alloys on annealing at 300° C.

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* Aluminum Research Laboratories, Aluminum Co. of America, Cleveland, Ohio.

[1] References are at the end of the paper.

Preparation and Chemical Analysis of Alloys

Electrolytically refined aluminum[7] and refined bismuth (99.993 per cent) were used in the preparation of the alloys for this investigation. Spectroscopically pure (99.9999 per cent) lead was used for the solidus determinations of the aluminum-lead alloys. Lead of somewhat lower purity was used in the solubility determinations. The analyses of the alloys are given in Tables 1 to 7, inclusive. As indicated in these tables, some contamination from silicon occurred in melts containing high concentrations of lead or bismuth, which necessitated high melting temperatures. For thermal analysis, sufficient aluminum for 200 to 500 grams of alloy was melted in small fire-clay, plumbago, or silicon carbide crucibles about 8 cm. in diameter by 13 cm. deep. Carbon crucibles about 4.8 cm. in diameter by about 9.7 cm. deep were used in solidus determinations. After the aluminum was melted, the lead or bismuth was added and the melt brought up to a temperature estimated to be well above the solubility temperature of the alloy concentration concerned. The melt was held for approximately 30 min. with constant agitation. A sample for chemical analysis was poured from the crucible into a cold iron mold, which gave a casting of about 75 by 40 by 5 mm. The mold is designed so that the 40-mm. dimension is in a vertical plane.

The melts used for determining the solubility by analyzing samples taken from the melt in equilibrium with the precipitated metal weighed 13 to 23 kg. The aluminum-lead alloys were melted in plumbago crucibles about 25.4 cm. in diameter by 35.6 cm. high. The aluminum-bismuth alloys could not be melted in plumbago crucibles because of the attack by the bismuth; they were melted in silicon carbide crucibles of about the same size as the plumbago crucibles.

Chemical Analysis.—The chemical analyses were obtained on drillings from the chill-cast slab and examination was made of the tendency of the alloys to segregate in this type of casting. The composition was found to be satisfactorily uniform in the lower three-fourths of the casting. There was a slight tendency for the surface to be somewhat low in alloy content. Samples were obtained by drilling all the way through the casting throughout the lower three-fourths of the specimen. The drillings were carefully mixed and subdivided in obtaining the analysis sample.

Thermal Analysis

Most of the cooling curves were determined with 500-gram melts, utilizing the relatively thick-walled plumbago or silicon carbide crucibles. The cooling rate varied somewhat with the concentration of lead or bismuth in the alloy between about 2° and 5° C. per minute. Temperatures were determined with 22-gauge chromel-alumel thermocouples and a precision potentiometer. The thermocouples were

standardized against the freezing point of pure aluminum before each run. In some cases they were standardized after the run as well. The

Table 1.—*Chemical Analyses and Thermal Points of Aluminum-lead Alloys*

Chemical Analyses, Per Cent								Primary Point, Deg. C.
Lead	Copper	Silicon	Iron	Zinc	Tin	Bismuth	Antimony	
0.99								
1.52								
1.70								673
1.75								674
2.11								699
3.15								752
3.16								750.5
3.75								776
4.27	0.02	0.08	0.02	0.00	0.00	0.00	0.05	794
4.27								794
6.43	0.02	0.03	0.03	0.00	0.05	0.00	0.04	861.5
7.07								883
8.70		0.27			0.10			917
10.63	0.02	0.35	0.02	0.00	0.11	0.00	0.02	950
3.57	0.01	0.01	0.02	0.00	0.00	0.00	0.07	658.65[a]
6.73	0.02	0.02	0.03	0.00	0.00	0.00	0.04	658.50[a]
3.97	0.01	0.00	0.01	0.00	0.00	0.00	0.06	658.40[a]

[a] Aluminum solidification points.

Table 2.—*Composition of Aluminum-lead Solubility Samples from Settling Experiment*

Temperature of Equilibrium, Deg. C.	Composition, Per Cent							
	Lead	Copper	Silicon	Iron	Zinc	Tin	Bismuth	Antimony
1,038	14.75							
984	12.33							
958	12.18							
927	11.50				0.25			
898	8.54							
867	7.02							
844.5	5.85							
814	4.87							
782	3.82							
764.5	3.47							
732	2.80	0.03	0.01	0.02	0.30	0.00	0.00	0.02
710	2.29							
673	1.92							

maximum difference observed in the thermocouples before and after a run was about 0.015 mv. This procedure gave satisfactory although weak points, indicating the heat evolved on passing from the field of one to two liquid layers.

The cooling curves determined by the technique just described were not considered satisfactory in the region of the aluminum-rich solidus. The changes in direction of the curves were not sharp, therefore it was

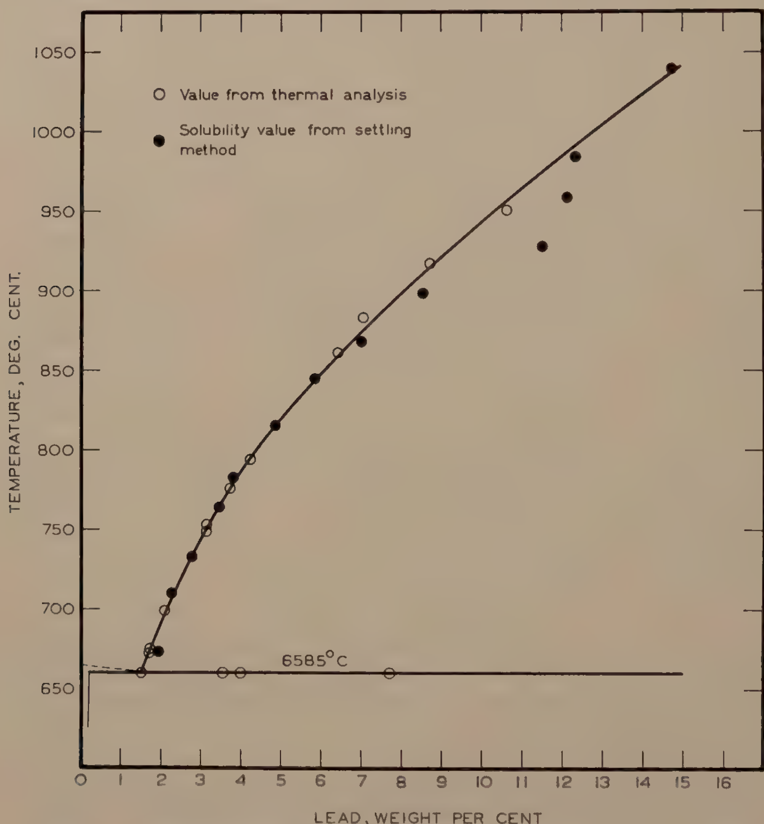

FIG. 1.—CONSTITUTIONAL RELATIONSHIPS IN ALUMINUM-LEAD ALLOYS.

difficult to deduce from them the temperature of solidification of the aluminum-rich liquid. Although the primary purpose of the investigation was the determination of the liquid solubility of lead and bismuth in aluminum, it appeared desirable to determine with greater accuracy the temperature of solidification of the aluminum-rich liquid in the two systems. It having been suggested that solidification might be taking place near the walls of the crucibles appreciably before the central portion was frozen, the shape and material of the crucible was changed. Relatively thin-walled carbon crucibles with a higher ratio of diameter to

height were used. These crucibles were also fitted with covers and had a capacity of about 200 grams of metal as compared with the 500 grams of the larger crucibles. The other equipment was the same as described in the foregoing. With the revised technique, sharp breaks were obtained at the solidus points and the solidification temperature of aluminum was found to be lowered about 1.5° C. by the addition of lead and about 2.9° C. by the addition of bismuth. The results of the thermal analyses are given in Tables 1, 3 and 6 and are plotted in Figs. 1, 2 and 3.

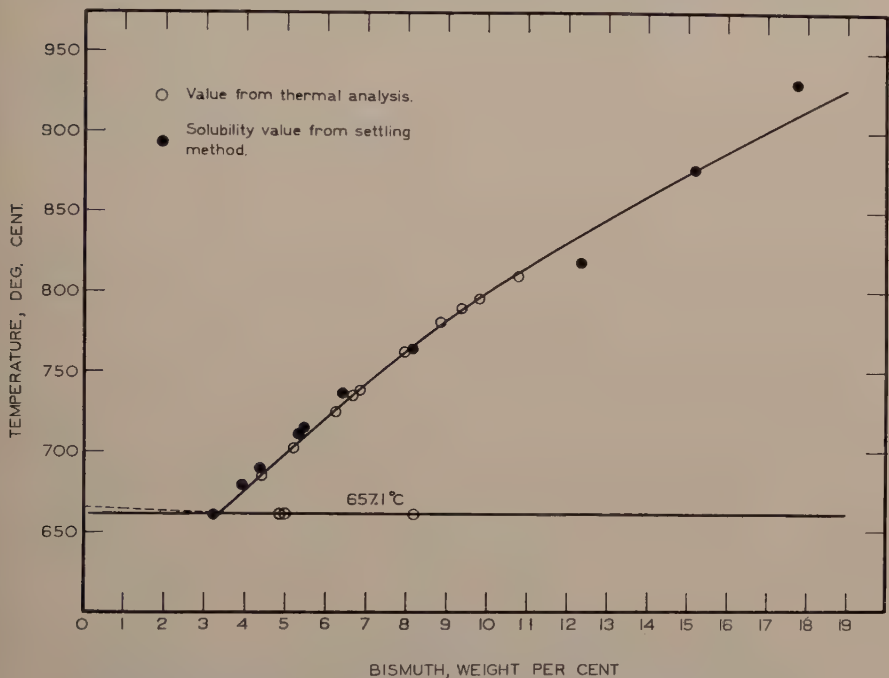

FIG. 2.—CONSTITUTIONAL RELATIONSHIPS IN ALUMINUM-BISMUTH ALLOYS.

SOLUBILITY BY CHEMICAL ANALYSIS

The smallness of the heat evolutions in the thermal analyses tended to decrease the accuracy of the results and, since there was some question of the amount of possible undercooling, it was decided to attempt to determine the solubility curves by means of chemical analyses of samples taken at specific temperatures from aluminum-rich melts in equilibrium with precipitated lead-rich or bismuth-rich melts. A typical procedure followed in making these determinations for the aluminum-lead and aluminum-bismuth systems will be described.

A quantity of high-purity aluminum weighing 13.6 kg. was melted in a plumbago crucible and heated to 1050° C., at which temperature 2.39 kg. of lead was added and the charge was stirred vigorously and

continuously until the temperature had again reached 1050° C. Analysis samples were taken and the crucible containing the charge was then transferred to an electric resistor furnace preheated to about 1050° C. The temperature controls of the electric furnace were set at 1000° C. After the charge had stood without disturbance for about an hour, the temperature of the melt near the surface was taken with a bare standardized chromel-alumel couple and samples for chemical analysis were carefully taken from the surface of the melt with a preheated ladle.

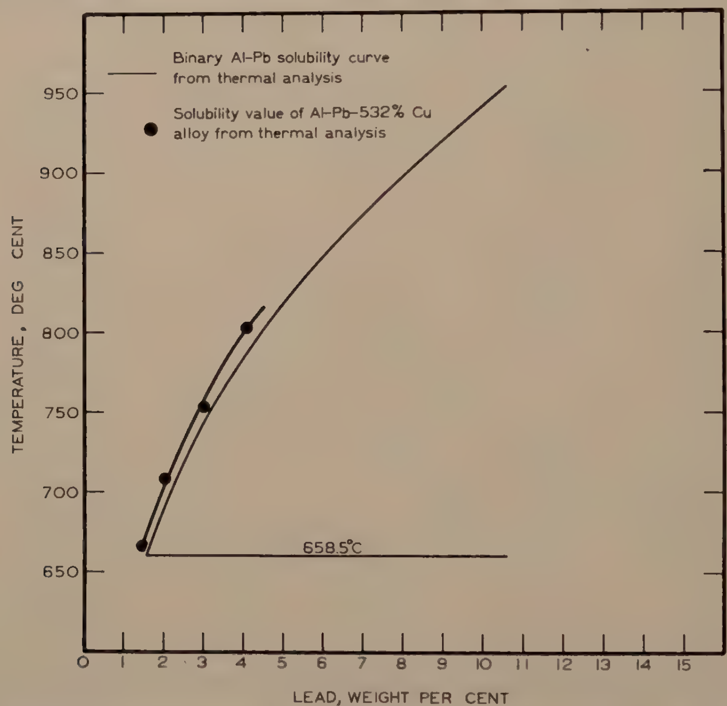

FIG. 3.—SOLUBILITY OF LEAD IN AN ALUMINUM ALLOY CONTAINING 5.3 PER CENT CU.

The temperature control of the electric furnace was then adjusted to allow a temperature drop of about 25° C. This temperature drop occurred in about 30 min. The charge was then held for about 2 hr. at this temperature and samples for analysis again carefully taken with as little disturbance of the melt as possible. This was repeated at successively lower intervals of 25° C., until the solidification point of the aluminum was almost reached. The melt was finally allowed to solidify and drillings were taken from the top center portion of the solidified regulus. All the samples were then chemically analyzed for lead and bismuth. The impurity content was checked as well. Preliminary experiments had indicated that equilibrium between the lead or bismuth and aluminum was quickly attained on the reduction of the temperature. The large

difference in specific gravity between the lead and bismuth and aluminum was probably responsible for the relatively quick and complete settling

TABLE 3.—*Chemical Analyses and Thermal Points of Aluminum-bismuth Alloys*

Composition, Per Cent				Primary Point, Deg. C.
Bismuth	Copper	Silicon	Iron	
1.13				
2.00				
3.40				
3.41				
3.44				
3.56				
4.41	0.02	0.01	0.02	685
5.21				702
6.23	0.02	0.01	0.02	725
6.66				735
6.84				738
7.94				762.4
8.81				782
9.36				789
9.80				795.5
10.77	0.03	0.03	0.01	810
4.84	0.01	0.01	0.02	657.1[a]
8.18	0.01	0.01	0.02	657.1[a]
5.05	0.00	0.01	0.00	657.2[a]

[a] Aluminum solidification point.

TABLE 4.—*Composition of Aluminum-bismuth Solubility Samples from Settling Experiment*

Temperature of Equilibrium, Deg. C.	Composition, Per Cent			
	Bismuth	Copper	Silicon	Iron
931	17.73			
877	15.19			
818	12.33	0.00	0.23	0.04
764	8.17			
737	6.41			
714	5.45			
710.5	5.32			
690.5	4.37			
679	3.94		0.24	
Solid sample surface drillings........	3.22			

out of the precipitated alloy. The results of these determinations are given in Tables 2, 4 and 5 and are plotted in Figs. 1, 2 and 4.

Solid Solubilities

The relatively high solubility of lead and bismuth in liquid aluminum at the freezing point suggested consideration of the solid solubility of these elements in aluminum. The aluminum-lead alloys were cast as ingots of about 3.8 by 17.8 by 20.3 cm. The castings were radiographed to insure ingots with uniform distribution of any undissolved constituents, after which the ingots were sectioned into four parts, 3.8 by 8.9 by 10.2

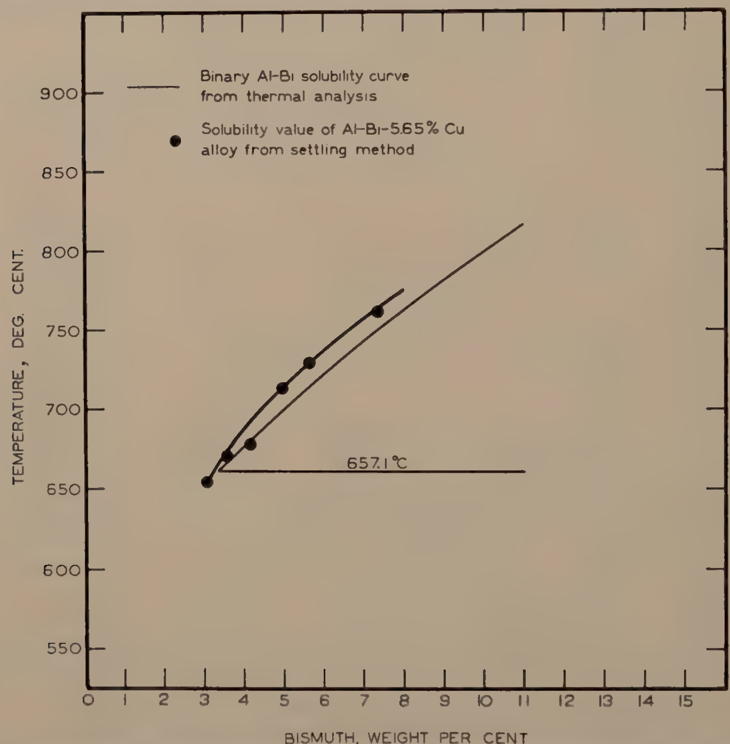

Fig. 4.—Solubility of bismuth in an aluminum alloy containing 5.65 per cent Cu.

cm., and the soundest section was cold-rolled to 0.95-cm. slab. The 0.95-cm. slabs, together with a similar slab of high-purity aluminum, were heated at 300° C. for 68 hr. and then cold-rolled to 18-gauge sheet. Specimens of sheet 0.95 by 50.8 cm. were prepared for investigation of the electrical resistivity as described by Fink and Willey.[8] The results of these determinations are given in Table 7 and are plotted in Fig. 5. A series of nine aluminum-bismuth alloys ranging from 0.24 to 4.07 per cent Bi were also similarly prepared in the form of 18-gauge sheet. Electrical resistivity measurements were not made on these alloys, however, since preliminary microscopic examination of the entire series after heating 388 hr. at 625° C. followed by 48 hr. at 650° C. revealed definite

evidence of bismuth out of solution in all specimens. A similar microscopic examination of the resistivity specimens also showed the lead to be out of solution in all alloys after heat-treatment at 610° C. for 19 hr. followed by heating for 89 hr. at 637° C.

Discussion of Results

These data indicate that the solubility of lead in liquid aluminum at the freezing point is about 1.52 per cent by weight and that this solubility increases with temperature to about 14.75 per cent at 1038° C. Similarly, the liquid solubility of the bismuth varies from about 3.36 per cent at the

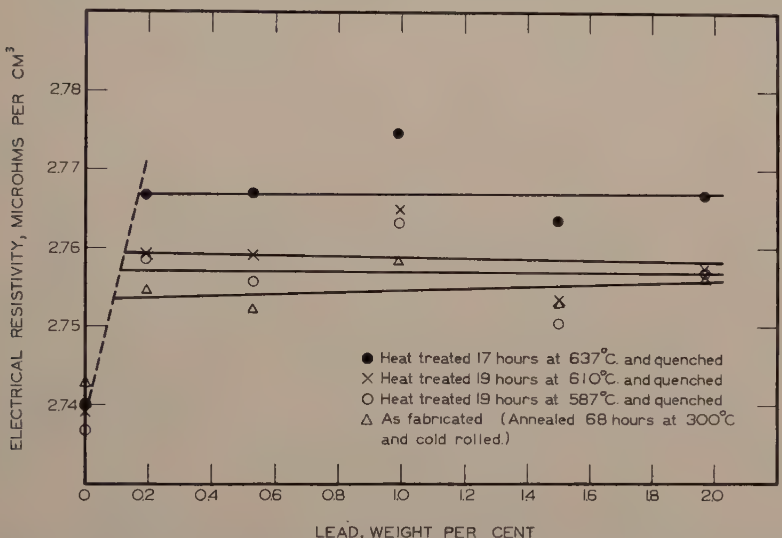

Fig. 5.—Electrical resistivity of aluminum-lead alloys as affected by heat-treatment.

freezing point of aluminum to about 15.19 per cent at 877° C. The freezing point of pure aluminum is lowered a maximum of 1.5° C. by the addition of lead and 2.9° C. by the addition of bismuth.

Utilizing Fink and Freche's[9] methods, the thermal data were plotted with the log of atomic concentration of the alloying element as one coordinate against the reciprocal of the absolute temperature. For the aluminum-bismuth system, the data, with the exception of one point at a low concentration of bismuth, lay along a straight line with a maximum deviation along the temperature axis of 3° C. and 0.2 per cent by weight of bismuth along the concentration axis. The average deviation of the data was far smaller than this. The data for the aluminum-lead alloys likewise fell satisfactorily along a straight line. The maximum deviation of the lead determinations from a straight line was somewhat greater than for bismuth, but the average deviation was of the same

order of magnitude. The results for the solubility by chemical analysis show considerably more scatter, particularly in the regions of high alloy concentration, than the results of a thermal analysis. In the lower portions of the aluminum-lead curve, the determinations of the solubility method lie somewhat above the curve obtained by thermal analyses. This suggests undercooling, which was disregarded in constructing the solubility curve, inasmuch as in the higher concentrations the solu-

TABLE 5.—*Composition of Aluminum-bismuth-copper Solubility Samples from Settling Experiment*

Temperature of Equilibrium, Deg. C.	Composition, Per Cent			
	Bismuth	Copper	Silicon	Iron
761	7.32	5.56	0.02	0.02
729	5.62	5.74		
713	4.97	5.82		
678	4.15	5.90		
671	3.59	5.98		
654	3.09	5.81		

TABLE 6.—*Chemical Analysis and Thermal Points of Aluminum-lead-copper Alloys*

Composition, Per Cent				Thermal Points, Deg. C.		
Lead	Copper	Silicon	Iron	Primary	Second	Aluminum Solidification
1.46	5.32			665.7	646.7	545.5
2.05[a]	5.32[a]	0.02[a]	0.01[a]	708[a]	646.7[a]	545.0[a]
3.04	5.32			753	646.7	545.3
4.10	5.35			802.5	646.7	544.8

[a] Zinc, 0.00 per cent; tin, 0.01; bismuth, 0.00; antimony, 0.06.

bility-by-analysis values tend to fall below the values determined by thermal analysis.

It is believed that, in general, the curves determined by the data on thermal analysis are somewhat the more reliable, particularly since the alloys utilized in this method were of somewhat higher purity and the results exhibit a higher degree of consistency. The solubility curves are extended, however, beyond the regions determined by thermal analysis to the higher concentrations utilized in solubility determinations according to the extrapolated $\frac{1}{T}$—$\log x'$ curves, inasmuch as these curves appear to be reasonable loci of the solubility points even in the higher concentrations of alloy.

Substituting the values for the lowering of the freezing point of the aluminum by lead or bismuth in the lowering of the freezing-point equation in Fink and Freche's paper,[9] and assuming a solid solubility of 0.1 per cent of each element in aluminum, the calculated solubility of lead in aluminum at the freezing point is about 1.7 per cent by weight. This is probably within the investigational error of the value determined experimentally (1.52 per cent Pb). The solubility of bismuth in aluminum at the freezing point is calculated to be 3.3 per cent by weight. This is in satisfactory agreement with the value 3.36 determined experimentally.

TABLE 7.—*Electrical Resistivity of Aluminum-lead Alloys*

Lead, Per Cent	Heat-treatment			
	68 Hr. at 300° C.[b]	19 Hr. at 587° C.	19 Hr. at 610° C.	17 Hr. at 637° C.
	Electrical Resistivity, Microhms per Cu. Cm.			
0	2.7427	2.7369	2.7390	2.7401
0.19[a]	2.7546	2.7588	2.7591	2.7668
0.53	2.7522	2.7558	2.7592	2.7669
0.99	2.7586	2.7633	2.7650	2.7746
1.50	2.7531	2.7506	2.7531	2.7634
1.97	2.7563	2.7573	2.7576	2.7667

[a] Copper, 0.02 per cent; silicon, 0.01; iron, 0.02; zinc, 0.02; tin, 0.00; bismuth, 0.00 and antimony, 0.02.

[b] Cooled in air at room temperature and cold-rolled approximately 90 per cent reduction.

It may be quite reliably assumed that both lead and bismuth are slightly soluble in solid aluminum but probably not to an extent greater than 0.2 per cent at the melting point of aluminum. The solubility apparently decreases with temperature. The data on the aluminum-copper-lead and aluminum-copper-bismuth alloys indicate both lead and bismuth to be slightly less soluble in aluminum containing about 5 per cent Cu than in pure aluminum. This decrease in solubility appears to be independent of the temperature in the ranges investigated and amounts to about 0.3 per cent for lead and about 0.6 per cent for bismuth (Figs. 3 and 4).

SUMMARY

1. The solubility of lead in liquid aluminum has been determined to be about 1.52 per cent at the freezing point of aluminum and to increase continuously with temperature to about 14.75 per cent Pb at 1038° C.

2. The solubility of bismuth in liquid aluminum has been determined to be about 3.36 per cent at the freezing point of aluminum and to increase with temperature to about 15.19 per cent at 877° C.

3. The freezing point of aluminum (660° C.) is lowered by the presence of lead to a minimum of 658.5° C. and by the presence of bismuth to 657.1° C.

4. The solubilities of lead and bismuth in solid aluminum have been found to be not more than about 0.2 per cent by weight, respectively, at the melting point of aluminum, and to decrease with temperature.

5. The solubilities of lead and bismuth in liquid aluminum are decreased slightly by the presence in the alloys of about 5 per cent Cu.

Acknowledgment

Indebtedness is gratefully acknowledged to Messrs. L. A. Willey, C. M. Tucker, and C. G. Jancura, who rendered valuable assistance throughout the investigation, and to Dr. A. J. Phillips, of the American Smelting and Refining Co., for the spectroscopically pure lead used in some of the solidus determinations.

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DISCUSSION

(*C. S. Barrett presiding*)

G. Edmunds,* Palmerton, Pa. (written discussion).—The higher lead and bismuth liquidus composition results determined by direct sampling of the melt, as compared to data obtained by thermal analysis, are contrary to general experience and lead one immediately to question the validity of the procedure used by Kempf and Van Horn.

In general, the determination of a liquidus point by direct sampling of the melt tends to place the point for any given composition at a higher temperature than the corresponding value as determined by a cooling curve. This is because the direct sampling can be done while the melt is at equilibrium; whereas the determination by the cooling-curve method depends upon a heat evolution, the temperature of which may be, and often is, significantly depressed.

The authors seem to have used a reasonable procedure in bringing their melts for the settling experiments to equilibrium. Proof of this, however, should have been obtained, for example, by the analysis of a second sample taken after the melt

* Research Division, New Jersey Zinc Co.

had stood for a further period at constant temperature. Failure to have reached equilibrium when approaching it, as in this case, from higher temperatures would have resulted in error in the direction of the observed difference between the results of cooling-curve and settling-method determinations.

The authors state that "After the charge had stood without disturbance for about an hour . . . samples for chemical analysis were carefully taken from the surface of the melt with a preheated ladle." One must presume the metal for analysis was poured from the ladle into an iron mold and the sample obtained on drillings in the same manner as is described on the second page of the paper. There it is pointed out that segregation occurred and that only drillings from the bottom three-fourths of the slab were used for analysis. This procedure would obviously yield results high in lead or bismuth, corresponding to the observed differences between the cooling-curve and settling-method data. Low results are possible due to segregation in the ladle if during transfer the metal cools and not all of it is cast, but this may be beside the point since the authors seem not to have been troubled with low lead or bismuth results. A simple way of avoiding errors due to segregation is to dissolve the entire sample and to analyze an aliquot.

A number of liquidus determinations have been made by direct sampling of melts of zinc alloys in the laboratory of The New Jersey Zinc Co. In these the entire sample has been used for analysis. Equilibrium has in many cases been approached from both supersaturated and undersaturated melts and results that check within the combined limits of temperature control and analytical error are consistently obtained. Nearly all of the liquidus points thus obtained have been found to lie at higher temperatures than corresponding points determined by cooling curves and to lie along straight lines when plotted as log of atomic concentration versus reciprocal of absolute temperature.

The sampling procedure used on zinc alloys has not always been the same, but a highly satisfactory one has been to break a teat from an evacuated Pyrex or silica bulb beneath the surface of the melt, the sample being sucked into the evacuated bulb. The bulbs used are of such a size as to contain an amount of alloy suitable for analysis. The sampling bulbs are placed in the melt long enough before sampling to insure their not needlessly disturbing the melt or its temperature. For metals in which Pyrex or silica would not be useful, the sample could well be drawn into a pipette made from graphite or other suitable material by much the same method. By having the opening through which the metal enters, when the teat is broken, at the top of the bulb no loss of sample will occur during removal of the bulb from the melt. The sample may be drawn into the bulb by partial vacuum in an attached tube, thus avoiding the necessity for employing a material that will hold a high vacuum.

L. W. Kempf and K. R. Van Horn (written discussion).—Mr. Edmunds questions the construction of the liquid-solubility curves with points determined by thermal analysis rather than those obtained by the direct sampling of the melt. He states that our direct sampling values occur at a lower temperature for a given composition than corresponding thermal-analysis values, whereas the reverse would be expected. We should like to point out that in the lower composition range of the aluminum-lead and the aluminum-bismuth liquid-solubility curves, the direct sampling values lie somewhat above the curve established by thermal-analysis data. Mr. Edmunds probably refers to only a few direct sampling values of higher lead composition in the aluminum-lead diagram. Experimental procedures with the sampling method became relatively difficult at these concentrations and temperatures with a considerably higher probable error in the results. Higher values of the solubility by chemical analysis than are obtained by thermal analysis for any particular composition suggest undercooling of the melts in the thermal determinations, and must be given consideration,

although no evidence of undercooling could be noted in the thermal data. It is doubtful whether the difference between the two sets of results in the lower range of concentration and temperature is greater than the experimental error. We preferred the thermal data because of the higher degree of purity of the alloys used in this phase of the work.

Mr. Edmunds suggests that the reason some of our values determined by direct sampling contain higher lead or bismuth than those determined by thermal analysis for a given temperature is that the melts were not held for a sufficiently long time at temperature before samples were taken. The space allotted for publication did not permit a description of the preliminary experiments necessary to establish a satisfactory procedure for the solubility by chemical analysis method. Tests at different temperatures holding the melt for various periods of time from 1 to 10 hr. showed no variations in concentration after holding for a period of at least one hour. Consequently, a procedure of slowly attaining a given temperature and a holding time of one hour was established for all direct sampling determinations of aluminum-lead and aluminum-bismuth alloys. The large difference in specific gravity between lead and bismuth and aluminum is probably responsible for the relatively quick and complete settling out of the precipitated alloy.

The paper describes the manner in which the chemical analysis slab was taken for any composition. As segregation occurred, only drillings from the bottom three-fourths of the slab were used for chemical analysis. Mr. Edmunds questions this procedure and suggests that this may be the source of the high values for lead and bismuth solubility obtained by the direct sampling of certain alloys. Inasmuch as the same method of chemical sectioning and analysis was employed for both thermal and the direct sampling specimens, all the results would be subject to the same error. It is difficult to explain, on the basis of Mr. Edmunds' suggestion, why the majority of the values determined by the sampling method have a lower lead or bismuth content for a given temperature than corresponding thermal data. Mr. Edmunds prefers the procedure of dissolving the entire sample and analyzing an aliquot. The aliquot method is also subject to errors, and it is a matter of opinion as to which method might yield the most satisfactory results.

Age-hardening of Duralumin

By Morris Cohen,* Junior Member A.I.M.E.

(Detroit Meeting, October, 1938)

Within the past two years, a number of publications have called attention to the double peaks, or stages, that appear in the hardness and strength curves of certain aging alloys. The author has shown the existence of double hardness peaks during the aging of a high-purity silver-copper alloy;[1] and on the basis of electrical resistance, microscopic, dilation and lattice-parameter measurements, he concluded that the initial hardness peak occurs prior to precipitation while the secondary hardening is due to precipitation. It was suggested that the general mechanism of age-hardening involves two consecutive processes, the first consisting of nucleus or knot[2] formation, and the second consisting of actual precipitation and particle growth. It was further held that the two stages are interdependent, but because of nonuniform precipitation they may overlap each other to an extent that increases as the aging temperature is raised. At high aging temperatures, the effect of the first stage cannot be detected because of the rapid occurrence of precipitation.

The general theory of age-hardening recently presented by Dr. M. L. V. Gayler[3] is in close agreement with the picture outlined above. With reference to work done on duralumin, copper-beryllium and copper-silver alloys, Dr. Gayler also concluded that age-hardening takes place in two consecutive steps: first, diffusion (in which the solute atoms migrate to certain crystallographic planes), and then precipitation.

However, W. L. Fink and D. W. Smith[4] have shown that the double aging peaks that appear in the strength curves of high-purity aluminum-copper alloys may be explained without recourse to pre-precipitation phenomena. By means of very careful metallographic technique, Fink and Smith demonstrated that during aging the precipitation takes place at an accelerated rate along the grain boundaries and slip planes as a result of the plastic deformation caused by the drastic quench from the solution heat-treatment temperature.† The general precipitation occurs at a

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* Assistant Professor, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

[1] References are at the end of the paper.

† This effect of quenching strains has been confirmed by G. Wassermann.[5] However, the latter believes that the resultant plastic deformation is a process of twinning rather than translation, and that the accelerated precipitation takes place along twinning planes instead of slip planes.

considerably slower rate in regions that do not undergo such plastic deformation. Consequently, these investigators concluded that the first aging peak is due to rapid precipitation in the localized regions that have experienced plastic deformation during quenching, and that the secondary hardening is the result of the subsequent general precipitation.

It is evident that the main difference of opinion between Dr. Gayler and the author, on the one hand, and Messrs. Fink and Smith, on the other, lies in the explanation of the initial hardening stage: i.e., pre-precipitation vs. localized precipitation. However, there need be no conflict between these two concepts in view of the fact that they are based on different alloys. Thus it may be argued that in some aging systems the initial hardening takes place prior to precipitation, while in others it is due to rapid localized precipitation. Furthermore, since the occurrence of either phenomenon does not preclude the possibility of the other, it is quite conceivable that in some age-hardenable alloys both may take place in addition to the general precipitation. As a matter of fact, some preliminary work carried out by the author three years ago indicated that all three processes may actually occur in duralumin to a greater or less degree, depending on the aging temperature.

Accordingly, the aging characteristics of a duralumin alloy were carefully reinvestigated by means of hardness, electrical resistance, microscopic, dilation and lattice-parameter measurements during aging at five temperatures. The preliminary findings were confirmed, and it is believed that the results lead to a general picture of age-hardening in which nucleus formation, localized precipitation and general precipitation may play important roles.

Experimental Details

The duralumin used for this investigation was received in the form of ¾-in. rods, which had been extruded and then cold-drawn. The composition of the alloy was found to be: copper, 4.19 per cent; magnesium, 0.58; silicon, 0.14; manganese, 0.63; iron, 0.32; chromium, 0.08.

Disks ¼ in. thick were cut from the rods for the hardness, microscopic and X-ray studies. The dilatometer specimens consisted of rods ¼ in. in diameter by 4 in. long, which were turned down from the original stock. The specimens for the electrical resistance measurements were in the form of wires made by drawing one of the dilatometer rods down to approximately 0.025-in. diameter.

Prior to aging all of the specimens were heated for 2 hr. at 515° ± 5° C. for the solution heat-treatment, and were then quenched in water at about 20° C. Aging studies were made at 30°, 65°, 100°, 150° and 191° C. An oil thermostat was used for the two lower aging temperatures, and oil baths heated by boiling liquids with suitable boiling points were

used for the three higher temperatures. The aging temperatures were controlled to ±0.5° C. All of the measurements on the aging specimens except the dilation were carried out at room temperature. The aging was interrupted by quenching in water at suitable intervals for these measurements, and then the specimens were returned to aging baths until the time for the next measurements. The dilation runs were not interrupted because these measurements could be readily made while the specimens were at the aging temperatures.

The hardness was measured with a Rockwell hardness testing machine using a 1/16-in. ball indentor and a load of 100 kg. (scale B). At least three determinations were made after each aging interval, and the hardness machine was checked before each set of readings with a standard hardness block.

The electrical resistance measurements were made in an oil thermostat at 25° C. with a Leeds and Northrup Kelvin bridge. The current and potential clamps were not removed from the specimens during the aging runs, so that changes in resistance of ±0.05 per cent could be detected.

The polishing and etching for the microscopic studies of aging specimens were performed with extreme care, in order to prevent surface flow and distortion of the structure. After trying a number of etching reagents, it was decided that the most satisfactory results were obtained with a 1/4 per cent hydrofluoric acid solution in water. The photomicrographs were taken with a Zeiss Neophot.

The dilation during aging was determined in a dilatometer described by the American Society for Testing Materials.[6] The changes in length could be measured to ±0.00001 inch.

The lattice-parameter measurements were made on surfaces that were polished prior to the solution heat-treatment. No further polishing or etching was done during the course of aging. A back-reflection camera and copper radiation were used. The camera and X-ray tube have been described by J. T. Norton.[7] The experimental error was approximately ±0.0002Å.

Discussion of Results

The results of the hardness, electrical resistance, dilation and lattice-parameter measurements are plotted as aging curves in Figs. 1 to 5. The initial values given for each aging temperature are those obtained on the specimens as quenched from the solution heat-treatment. The principal changes in microstructure are shown in Figs. 7 to 10.

The hardness curves indicate that the age-hardening of this duralumin alloy is basically a three-step process. At aging temperatures of 150° and 191° C., the three stages in the hardness curves are evident. Because of the lower rates of aging at 65° and 100° C., only the first two stages are observed within the duration of the tests, while at 30° C. only the first

stage is noted.* Further evidence of the consistent nature of this complex hardening process is given in Fig. 6, in which the reciprocal of the absolute aging temperature is plotted against the logarithm of the times required to attain the maximum hardness and also the begin-

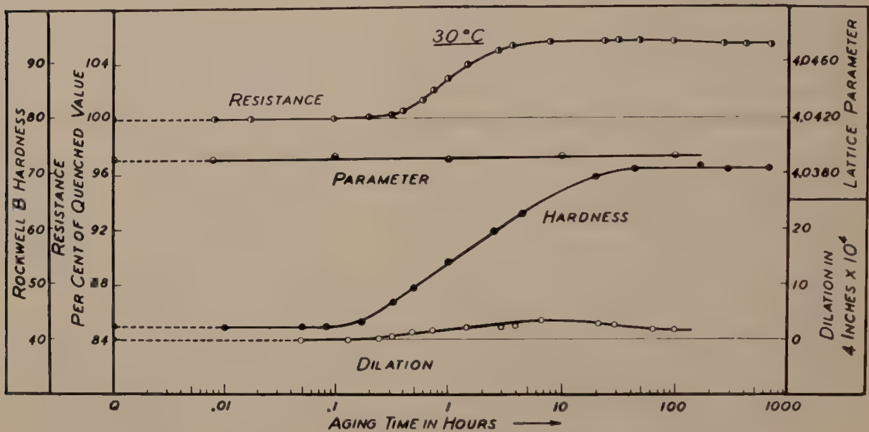

Fig. 1.—Aging curves of duralumin alloy at 30° C.

ning of each hardening stage. The four points representing the beginning of the second stage lie on a straight line. While only two points are available for each of the other stages, the straight lines drawn between

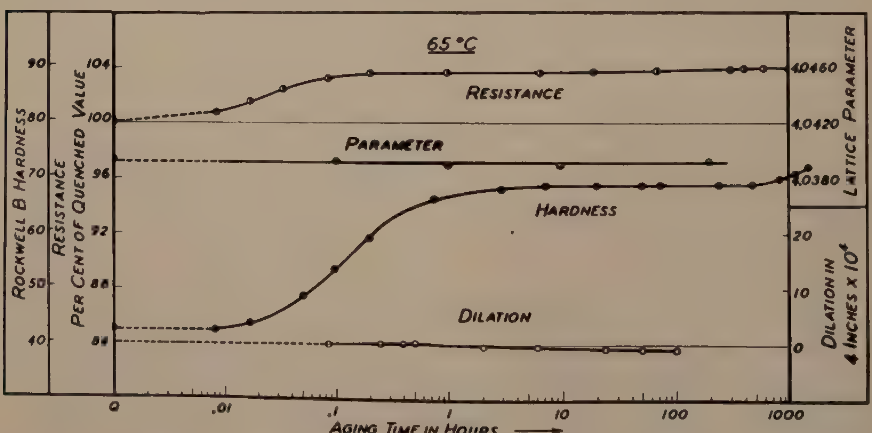

Fig. 2.—Aging curves of duralumin alloy at 65° C.

these points demonstrate a very consistent trend, and indicate that the three hardness stages are probably due to related, not independent, processes. It is interesting to note that if these lines are extrapolated

* A single hardness run made at 250° C. showed only the last two stages, the aging being so rapid that the initial stage could not be detected.

back to lower temperatures, it may be determined that at room temperature this duralumin alloy will reach the second hardness stage in about 35 years, the third hardness stage in 100,000 years and maximum hardness in 10,000,000 years!

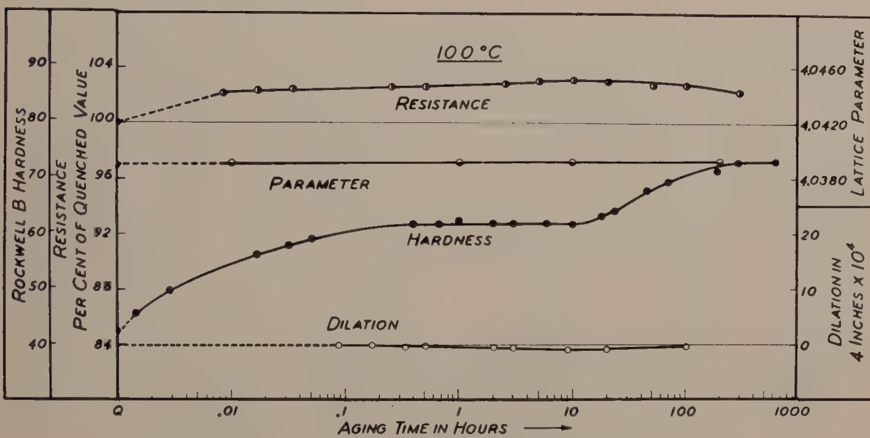

FIG. 3.—AGING CURVES OF DURALUMIN ALLOY AT 100° C.

At all the aging temperatures studied, the initial hardening is accompanied by a large increase in electrical resistance. The extent of this increase becomes greater at the lower aging temperatures, reaching a value 5.6 per cent above the quenched resistance on aging at 30°. The

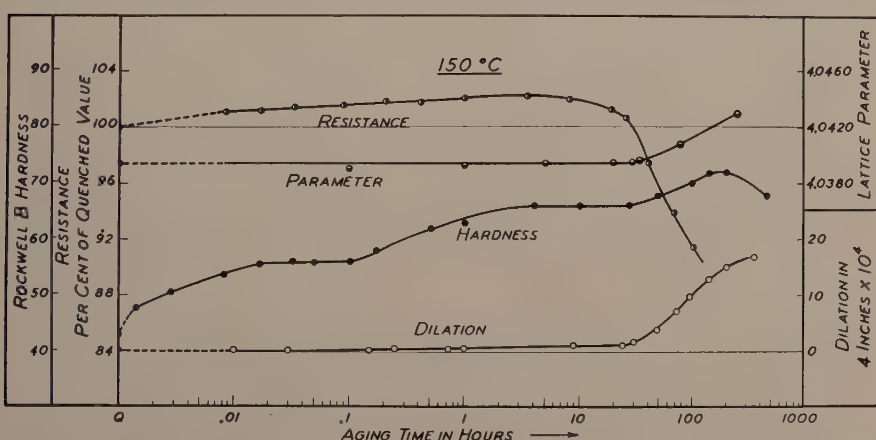

FIG. 4.—AGING CURVES OF DURALUMIN ALLOY AT 150° C.

hardness attained during the first stage also increases as the aging temperature is lowered. It is believed that the large increase in resistance is indicative of the lattice distortion that results from the formation of nuclei within the supersaturated solid solution in preparation for the precipitation of $CuAl_2$.

The dilation curves at 30° and 65° show an initial expansion and a subsequent contraction, both of which take place during the first hardening stage. The two effects seem to overlap and tend to mask each other.

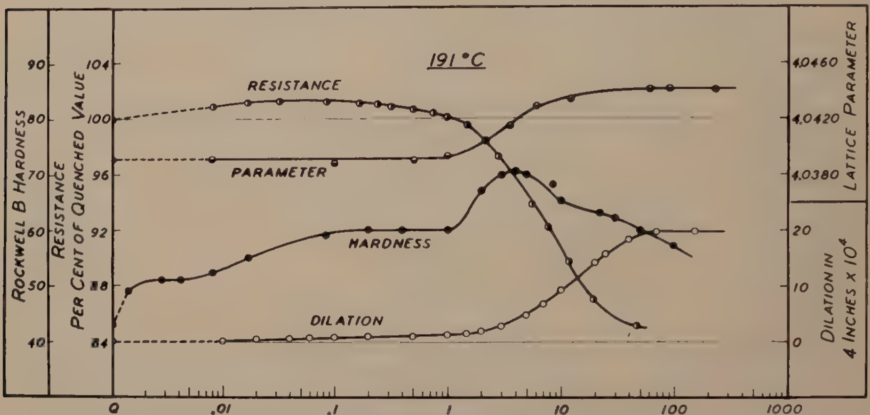

FIG. 5.—AGING CURVES OF DURALUMIN ALLOY AT 191° C.

As the aging temperature is raised these initial changes in length occur very rapidly. At 100°, the first expansion cannot be detected, and at 150°

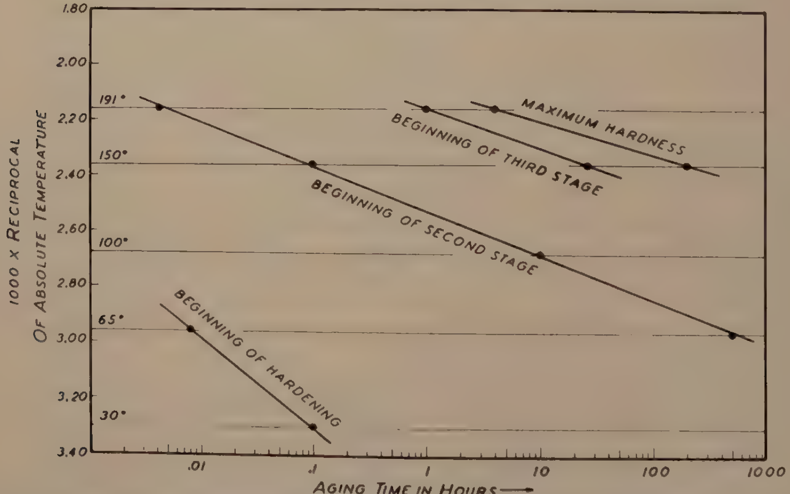

FIG. 6.—RELATIONSHIP BETWEEN AGING TEMPERATURE AND TIME REQUIRED TO ATTAIN THE VARIOUS HARDENING STAGES.

even the contraction cannot be detected. These results are in close agreement with the curves published by I. Igarasi[8] for a duralumin alloy containing copper 4.02, magnesium 0.76, silicon 0.69, manganese 0.32, and iron 0.85 per cent. The real significance of the expansion is open to

question. The precipitation of some phase such as $CuAl_2$,* Mg_2Si or a complex compound would cause an expansion. However, the precipitation of $CuAl_2$ in this early stage is unlikely, first because of the large increase in electrical resistance at this time, and secondly because binary

Fig. 7. As quenched from 515° C. Fig. 8. Aged 6 minutes.

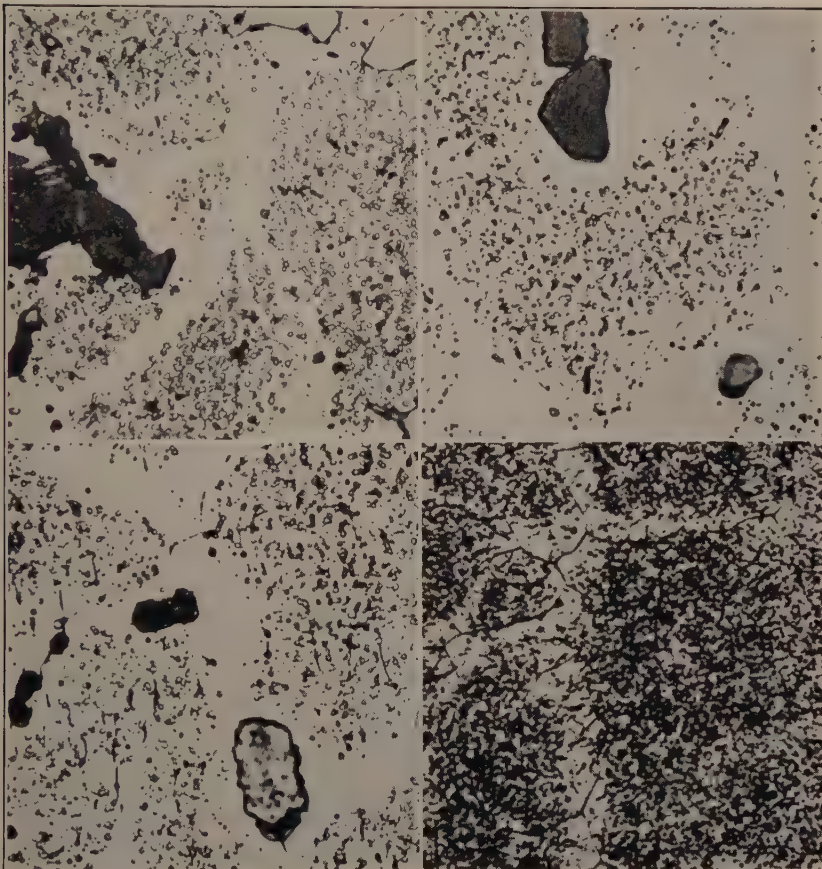

Fig. 9. Aged 1 hour. Fig. 10. Aged 24 hours.

FIGS. 7–10.—CHANGES IN MICROSTRUCTURE DURING AGING AT 191° C. ETCHED WITH ¼ PER CENT HYDROFLUORIC ACID IN WATER.

Zeiss Objective, Apochromat 90 Oil. Eyepiece, Homal IV. N.A. = 1.30. × 2000.

aluminum-copper alloys actually contract[8,12] instead of expand during room-temperature aging. Igarasi has also shown[8] that ternary

* In the present discussion of precipitating phases, no attempt is made to distinguish between the possible metastable phases[5,9,10] and the corresponding stable compounds. It is recognized that transition structures in precipitates are common. However, they are quite persistent once formed, and certainly would not complicate matters by suddenly transforming to the stable state within the course of these experiments.[5,11]

aluminum-magnesium-silicon alloys expand during aging at room temperature, probably because of the precipitation of Mg_2Si; but this expansion even in the high-magnesium silicide alloys is much smaller than that found for duralumin in spite of the low Mg_2Si content of the latter.* Therefore the precipitation of Mg_2Si cannot account for the initial expansion of the duralumin. By a process of elimination, then, it appears that the expansion may be due to the precipitation of a complex phase, perhaps the Al-Cu-Mg-Si compound mentioned by E. H. Dix[13] and again by D. A. Petrov.[14]

However, it turns out that this precipitation—if it occurs at all—can have little bearing on the basic age-hardening process, as demonstrated by the following experiment. Specimens for hardness and dilation measurements were overaged at 191° C. then reheated to 515° C. for barely enough time to attain the temperature, and quickly quenched. The hardness sample showed very little increase in hardness on aging at 30° C. This indicated that the time at the high temperature was insufficient to dissolve an appreciable amount of the hardening constituent. Yet the dilation specimen on aging at 30° displayed the same expansion as when it had received the 2-hr. solution heat-treatment. The subsequent contraction, however, was not observed. In view of the fact that the expansion may occur without the hardening of the duralumin, it seems certain that this expansion is not caused by the same aging process that causes the hardening. Hence, whether the initial expansion is the result of the precipitation of a complex compound or is simply due to the relief of quenching strains, it can be said that the source of this expansion is not a significant factor in the basic hardening mechanism. On the other hand, the contraction (which evidently *is* related to the hardening process because the contraction does not occur without the hardening) is believed to be the same in origin as the contraction found during the room-temperature aging of the binary aluminum-copper alloys, and therefore gives further evidence of the lattice strain caused by nucleus formation prior to the actual precipitation of $CuAl_2$.

No changes in lattice parameter or microstructure occur during the initial hardening. The microscopic investigation of this duralumin alloy was not entirely satisfactory because of the complexity of the microstructures. Even in the quenched condition, the structure contains a finely divided dispersoid in addition to many large inclusions (Fig. 7). In order to resolve the individual particles of the dispersoid, high magnification and extreme care in the polishing and etching are necessary. This dispersoid is apparently insoluble in the matrix, as indicated by the

* Calculated on the assumption that all of the silicon is combined with the magnesium, the duralumin under investigation contains 0.38 per cent Mg_2Si. This leaves 0.34 per cent excess magnesium.

fact that the size and distribution of the particles cannot be altered by a prolonged homogenization treatment or by a resolution heat-treatment after aging. Therefore it is believed that the fundamental mechanism of the aging process is little affected by the presence of these inclusions, although the inclusions probably influence the magnitude of the physical properties attained during aging and also tend to obscure the first evidences of precipitation.

It is important to note, however, that the dilute hydrofluoric acid etching reagent used does not reveal any grain boundaries in the matrix of the alloy in the quenched condition. The first structural change that can be detected during aging is the appearance of the grain boundaries in regions that contain no inclusions (Fig. 8). This always occurs during the secondary hardening stage. This grain-boundary etching attack is caused by localized precipitation, as proved on further aging by Fig. 9, in which the precipitated particles are resolved and additional grain boundaries are revealed even in the areas containing the dispersoid. The aging curves indicate that this precipitation process* counterbalances the effect of the nucleus formation going on within the grains and causes a gradual expansion (which should not be confused with the expansion previously discussed) as well as a moderate decrease in electrical resistance. Both of these reversals take place during the secondary hardening. The lattice parameter remains constant during these changes, but this anomaly is explained by the fact that the X-ray is very insensitive to the initial stages of localized precipitation.

During the third hardness stage, the etching characteristics of the alloy change completely. The microscope shows a darkening of the structure due to general precipitation, as in Fig. 10. This is verified by the marked expansion and the rapid decrease in resistance. The orders of magnitude of these changes are considerably greater than those that occur during the first two stages. The gradual rise in lattice parameter during the third stage is final substantiation of general precipitation.

In view of the complicated nature of this duralumin alloy and the fineness of the precipitated particles, the identity of the precipitated phase could not be determined metallographically. The existing literature on the constitution and age-hardening of aluminum-base alloys indicates that $CuAl_2$, Mg_2Si and a complex Al-Cu-Mg-Si compound[13,14] are phases that may be considered as possible precipitates. However, Mg_2Si may be ruled out as an important hardening constituent because the amount present† in the alloy is too low to have an appreciable effect, especially in the presence of excess magnesium.[15,16] Fortunately, a recent paper by L. W. Kempf and H. L. Hopkins[17] throws some light on the precipitation process. These investigators studied the changes in length of a high-

* No preferential precipitation was observed along crystallographic planes.

† See footnote on page 102.

purity aluminum copper alloy containing 10 per cent Cu. On aging at 193° C., this alloy exhibits a slight gradual expansion over a period of 1 to 2 hr., and then a rapid expansion, which reaches a maximum in 40 to 50 hr. This is exactly what is found for the duralumin alloy under discussion upon aging at 191° C. (Fig. 5). In addition, Kempf and Hopkins showed that grain-boundary precipitation in the high-purity alloy occurs during the small initial dilation, while general precipitation accompanies the rapid expansion. This is also found in the duralumin alloy. Evidently, then, the nature of the precipitation process in the complex duralumin alloy is very similar to that in the high-purity aluminum-copper alloy. Therefore it seems likely that, in duralumin, $CuAl_2$ is the predominant hardening constituent, and that the precipitation of this compound along the grain boundaries and later within the grains is responsible for the changes in length, resistance, lattice parameter and microstructure observed during the second and third hardening stages.

One may also assume that the pre-precipitation stage itself consists of two overlapping processes: (1) accelerated nucleus formation along the grain boundaries corresponding to the eventual localized precipitation, and (2) general nucleus formation within the grains corresponding to the eventual general precipitation. Such a concept seems reasonable, but in the present paper no attempt is made to distinguish between these possible stages, since no experimental evidence of a two-step pre-precipitation process was found.

It may be further mentioned that the three-stage hardening is not unique with this particular duralumin alloy. The same type of hardening was found in 17S duralumin on aging at 191° C. The latter contained: copper 3.98, magnesium 0.82, silicon 0.22, manganese 0.51, and iron 0.70 per cent. Apparently the basic mechanism of the age-hardening of duralumin is not altered by considerable variations in the composition. Of course, the rate of aging and the properties attained at each stage may be greatly affected by the composition of the alloy.

Conclusions

The basic aging mechanism of duralumin involves a pre-precipitation stage as well as actual precipitation. It is believed that the pre-precipitation stage is a process of nucleus formation in preparation for the precipitation of $CuAl_2$. However, when the precipitation occurs, it does not take place uniformly. Localized precipitation sets in first along the grain boundaries, and this is ultimately followed by general precipitation within the grains. The pre-precipitation stage is indicated by a slight contraction and a considerable increase in electrical resistance, but no change in microstructure or lattice parameter. The localized precipitation stage is characterized by a slight expansion, a modest decrease in resistance and a darkening of the grain boundaries, but still no change

in lattice parameter. The general precipitation stage is accompanied by a large expansion, a rapid decrease in resistance, a darkening of the whole microstructure and a change in lattice parameter. These three stages may overlap to a considerable degree, but they proceed at different rates and are sufficiently distinct in duralumin to result in three-step hardening. During the room-temperature aging of duralumin the hardening is essentially due to nucleus formation. Any actual precipitation that may occur at room temperature is incidental and not a vital factor in the hardening mechanism.

It is further suggested that this combination of nucleus formation, localized precipitation and general precipitation offers a comprehensive picture of the age-hardening process. Many modifications of this three-stage process are possible. For example, an aging system that undergoes uniform precipitation represents a special (and perhaps very rare) case in which there is no localized precipitation. Such an alloy would exhibit a two-stage hardening process, owing to nucleus formation and general precipitation. On the other hand, if the alloy is highly susceptible to plastic deformation during quenching, the localized precipitation stage may be emphasized because of the accelerated precipitation along the slip or twinning planes as well as at the grain boundaries. It is also conceivable that in some alloys localized precipitation may set in so rapidly that it obscures the evidence of the pre-precipitation stage in regions where general precipitation will eventually occur. This should result in two-stage hardening due to localized and then general precipitation although both precipitates are actually preceded by nucleus formation. Finally, if the precipitation is very nonuniform, the effects of the individual stages may overlap to such an extent that only a single hardness peak is found. One may visualize many additional variations and combinations of these processes.

Thus the occurrence of one, two or three hardening stages in the aging curves of alloy systems may all be explained on the basis of the general mechanism herein presented for the age-hardening of duralumin.

Acknowledgments

The author desires to express his appreciation to Mr. F. H. Gray, for his excellent work in the preparation of the specimens for microscopic examination, and to Dr. W. L. Fink and Dr. D. W. Smith, of the Aluminum Research Laboratories, through whose courtesy the chemical analyses were made.

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DISCUSSION

(*J. C. Jones presiding*)

W. L. Fink,* New Kensington, Pa. (written discussion).—It is gratifying to note that Dr. Cohen has verified the fact that preferential precipitation will produce a hardness peak, even though he used a complex alloy containing a chromium dispersoid, which rendered difficult the microscopic detection of the precipitate.

The complex nature of commercial duralumin also seriously interferes with interpretation of the hardness curves. For years there has been a controversy as to whether the age-hardening of duralumin at room temperature (Dr. Cohen's first hardening peak) is caused by the precipitation of Mg_2Si or $CuAl_2$. I do not believe that Dr. Cohen's reference to the behavior of the binary alloys settles this question, because added elements such as magnesium and iron markedly alter the aging characteristics of aluminum-copper alloys, and copper, silicon and magnesium markedly

* Aluminum Research Laboratories, Aluminum Company of America.

alter the aging characteristics of aluminum-magnesium-silicide alloys, nor do I believe that his reference to the change in electrical conductivity is convincing, because the modern theory of the structure of metals predicts that the first stages of precipitation should cause an increase in electrical resistivity rather than the decrease that Dr. Cohen assumes.

I hope that Dr. Cohen will attempt to find three aging peaks, using a binary aluminum-copper alloy. If knots of copper atoms harden duralumin, they should harden aluminum-copper alloys. Therefore, if Dr. Cohen's explanation were correct —that the first peak is caused by knots of copper atoms—it should be possible to find an earlier peak in the aging of aluminum-copper alloys.

I have been using the term "knots," which was introduced by Merica, to distinguish disordered groups of copper atoms on the aluminum lattice (products of pre-precipitation reaction) from nuclei (those minute particles of the second phase which are the first product of precipitation). Dr. Cohen used the terms "nuclei" and "knots" synonymously. I consider it unfortunate that the same term was used for such different things, especially when there are well established in the literature distinctive terms that symbolize the two theories of age-hardening—precipitation and pre-precipitation.

C. S. Barrett,* Pittsburgh, Pa. (written discussion).—It should simplify the interpretation of aging curves of the types discussed in this paper if the precipitation on slip planes were avoided. With thin specimens and with slower cooling velocities in the quenching process, it should be possible to eliminate all plastic flow on slip planes during quenching and remove this factor from the list that must be considered in explaining the complexities of the aging curves. A further simplification might result from eliminating grain-boundary effects by the use of single crystals, or at least very large-grained material.

M. L. V. Gayler,† Teddington, Middlesex, England (written discussion).—The author's observation that age-hardening of this alloy takes place in three stages is of particular interest. Recently, my colleague, G. D. Preston,[18] and simultaneously, Calvet, Jacquet and Guinier,[19] at the Collège de France, have shown, by specialized X-ray technique, that the early stages of aging of high-purity copper-aluminum alloys may be associated with segregation of copper atoms on the 100 planes of the crystal. This result is evidence in favor of the view which I have put forward[20] that the first stage of aging is due to the diffusion of solute atoms to planes about which precipitation proper ultimately takes place.

When duralumin is slowly cooled from a high temperature to room temperature, more than one phase is precipitated from solid solution, which would indicate that the aging of this alloy must be associated with the precipitation of these phases. The author has found that the first two of the three hardening processes, which he has observed in duralumin when aged at different temperatures, are accompanied by (1) no change in lattice parameter, (2) an increase in electrical resistivity; I would tentatively suggest that these two hardening processes have probably similar origins and that they are due to the segregation of more than one kind of atom onto planes of precipitation, the rate of segregation depending on the kind of atom and also on the temperature of aging. The fact that the X-ray analyses previously mentioned

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* Physicist, Metals Research Laboratory, Carnegie Institute of Technology.

† Metallurgy Department, National Physical Laboratory.

[18] G. D. Preston: *Nature* (1938) **142**, 570; *Proc.* Roy. Soc. (1938) **167**-A, 526.

[19] A. Guinier: *Nature* (1938) **142**, 569.

Calvet, Jacquet and Guinier: *Compt. rend.* (1938) **206** [26], 1972.

[20] M. L. V. Gayler: *Jnl.* Inst. Metals (1937) **60**, 249.

showed that a segregation of atoms takes place in the early stages of aging—a process that is accompanied by an increase in electrical resistivity but no change in lattice parameter—lends support to the above suggestion, which can be checked experimentally.

On page 98 the author remarks: "While only two points are available for each of the other stages, the straight lines drawn between these points demonstrate a very consistent trend, and indicate that the three hardness stages are probably due to related, not independent, processes." While I think the author's conclusion is probably correct, I fail to see how "straight lines drawn between *two* points" can do other than "demonstrate a very consistent trend!"

The fact that initial expansion and subsequent contraction take place on aging at 30° and 65° C., and that on aging at higher temperatures both these effects disappear, is most interesting. Preston and I[21] found that on aging an alloy containing 4 per cent Cu, 0.5 per cent Mg, 0.3 per cent Si, remainder Al, at room temperature and at 200° C., a change in density took place at the first temperature which corresponded with an initial expansion, within 4 hr., followed by a gradual expansion; while at 200° C. the density changes indicated a very marked expansion. It is pleasing that the author's results for the same duration of time are in agreement with these.

The interpretation of these volume changes must be left until our knowledge of the changes taking place within the lattice has expanded as a result of data obtained from X-ray examinations on the lines developed by Preston and Calvet, Jacquet and Guinier.

It is interesting that the dilatation of a specimen overaged at 191° C. and then reheated quickly to 515° C. and quenched is similar to that on aging at 30°, but that there is no subsequent contraction. The short treatment at 515° C. can hardly—as the author remarks—cause appreciable resolution of the precipitated phases.

It would seem more probable that this change was due to the relief of stresses set up after quenching. Phillips and Brick[22] have shown that if a quenched 5 per cent Cu-Al alloy is aged at 350° C., even after quenching from this aging temperature into cold and boiling water abnormal lattice parameter changes occur. These they have attributed to quenching strains.

With regard to the microscopic analysis, I cannot help wondering why the author did not use Keller's etching reagent, which has been so successfully used by Fink and Smith[23] for developing up structures in copper-aluminum alloys aged at different temperatures. The photomicrographs, Figs. 7 to 10, are not convincing. The presence of what the author calls "a finely divided dispersoid which cannot be altered by a prolonged homogenization treatment or by a resolution heat-treatment after aging," is disconcerting. I suggest that this dispersoid may be a polishing defect, for the following reason: one of the phases present in the microstructure of duralumin of composition cited by the author is a dove-gray constituent, which is definitely a manganese-rich constituent. Unless very great care is taken during polishing, this phase falls out, leaving cracks or holes near other phases. It is obviously, therefore, a very brittle substance and it is highly probable that the fine dispersoid is very fine pieces of this phase, which have been ground down during the polishing process and have become embedded in the softer matrix. The fact that heat-treatment has no effect on them is evidence in favor of this suggestion. The author remarks, page 103, "It is important to note, however, that dilute hydrofluoric acid . . . does not reveal any grain boundaries . . . in the quenched condition." A reagent commonly used for etching up grain boundaries in alloys of the duralumin type is 0.5 per cent hydro-

[21] Gayler and Preston: *Jnl.* Inst. Metals (1929) **41,** 191.

[22] Phillips and Brick: *Trans.* A.I.M.E. (1934) **111,** 94.

[23] W. L. Fink and D. W. Smith: *Tran.* A.I.M.E. (1936) **122,** 284.

chloric, and I would therefore like to ask the author whether he has found that a prolonged time of etching also fails to reveal grain boundaries in the quenched alloy? I am surprised, too, that "The first structural change that can be detected during aging is the appearance of grain boundaries in regions that contain no inclusions," for the first signs of aging generally appear *within* the grains and not in the grain boundaries. The etching reagent used by the author is one that hitherto has failed to reveal changes in microstructure accompanying the early stages of aging, and I would strongly recommend that the author try Keller's reagent after he has overcome the difficulty of the dispersoid—if possible!

M. Cohen (written discussion).—It is true that the theory presented in this paper for the age-hardening of duralumin would have been more straightforward if the work had been done on a high-purity binary aluminum-copper alloy. As a matter of fact, such an investigation will be undertaken shortly at the Institute. However, it should be emphasized that most of the aging studies on high-purity aluminum-base alloys are principally directed toward a better understanding of the aging mechanism in duralumin, and hence a careful determination of the aging characteristics of this complicated alloy forms an essential part of the long-range program.

As Dr. Fink suggests, the three-stage picture of the aging process put forth in this paper will be strengthened considerably if similar effects can be found in a binary aluminum-copper alloy. On the other hand, this picture will not be invalidated if three-step hardening cannot be detected in the binary alloy, because the softness of this material may prevent sufficiently sensitive hardness determinations, and excessive plastic deformation during the quench after the solution heat-treatment may cause the localized precipitation stage to obscure the hardening effect of the pre-precipitation stage. Dr. Barrett has proposed to eliminate the localized precipitation stage by using thin specimens and slower quenching velocities to prevent accelerated precipitation along the slip planes, and also by using single crystals to avoid grain-boundary precipitation. Unfortunately, both of these suggestions lead to difficulties in obtaining accurate hardness readings.

Dr. Fink has objected to my interpretation of the electric resistance changes during the aging of this duralumin alloy on the grounds that "modern theory of the structure of metals predicts that the first stages of precipitation should cause an increase in electrical resistivity rather than the decrease that Dr. Cohen assumes." My assumption is consistent with the experimentally determined fact that the electrical resistance of solid solutions decreases markedly as the concentration of the solute is decreased. Dr. Fink's opposite assumption is based on "modern theory," which to my knowledge has not yet been worked out for systems undergoing phase transformations.

Dr. Gayler's picture of copper atoms diffusing toward, and segregating on, the (100) planes of the matrix during the aging of binary aluminum-copper alloys is quite consistent with the nucleus or knot-formation stage to which I have attributed the initial hardening in duralumin. However, I cannot subscribe to her interpretation of the second hardening stage as another pre-precipitation process involving segregations of atoms other than copper. In my opinion, the amounts of impurities such as magnesium and silicon in this alloy are too small to produce such a large increase in hardness.

Dr. Gayler has obviously misunderstood my reference to the "consistent trend" shown by the lines in Fig. 6. This reference was intended to allude not to the straightness of the lines, but to the approximate parallelism of the lines.

I am in agreement with Dr. Gayler's explanation of the dilation found on aging at 30° after a short treatment at 515° C. The possibility of relieving quenching strains during the aging was mentioned on page 102. Dr. L. W. Kempf has reported that he has found such a dilation on "aging" a quenched specimen of pure aluminum,

which is further confirmation that the initial expansion found during the aging of duralumin is due to the relief of quenching strains rather than to some incidental precipitation process.

The metallographic polishing was done with extreme care, and it is very unlikely that the fine dispersoid is the result of defective polishing, as intimated by Dr. Gayler. In the first place, our polishing produced no such dispersoid in 17S duralumin. In the second place, specimens of the duralumin alloy described in this paper were sent to Dr. D. W. Smith, at the New Kensington Laboratories of the Aluminum Company of America, where the dispersoid was again found after careful polishing and etching. Unquestionably, this dispersoid is a part of the microstructure. Keller's etching reagent, as well as many others, was tried before it was found that dilute hydrofluoric acid gave most satisfactory results for our purpose. Some of the other reagents, including hydrochloric acid, brought out grain boundaries in the quenched alloy, but also attacked the dispersoid and left a very messy looking structure. Even the hydrofluoric acid must be used judiciously. Prolonged etching of the quenched alloy with dilute hydrofluoric acid will reveal the grain boundaries but not without obscuring the structure by "chewing out" the particles of the dispersoid.

Dr. Gayler mentions that the first metallographic signs of aging generally appear *within* the grains rather than at the grain boundaries. This is not in accord with our experience. All of the metallographic studies made here at M. I. T. on the age-hardening of aluminum-base, copper-base, silver-base and magnesium-base alloys have shown precipitation to take place first at the grain boundaries and later within the grains.

Effect of Plastic Deformation on the Age-hardening of Duralumin

By Robert W. Lindsay* and John T. Norton,† Member A.I.M.E.

(Detroit Meeting, October, 1938)

A number of detailed investigations of the physical changes accompanying age-hardening have raised the question as to the possibility of some phenomenon preceding the actual process of precipitation. There is considerable evidence to indicate that in the first stages of the aging process there is a pronounced distortion of the crystal lattice. This is particularly marked in duralumin. It would be of considerable theoretical interest to know the nature of this distortion as compared with that produced in other ways and to find out whether, in supersaturated alloys, it is a necessary antecedent to the formation of a second phase by precipitation. It was believed that a study of the age-hardening characteristics of a normally aged alloy compared with one that had been mechanically distorted might supply some useful information on these points. In addition, information would be obtained regarding the effect of a mechanical distortion on any subsequent stage in the aging process.

Duralumin was chosen as the material for this investigation because the various aspects of its aging behavior can be shown in detail by suitable variations of the aging temperature. Also, probably more work has been done on this class of alloys than on any other. In spite of the many published results, it was felt that the experiments would be significant only if all of the work were done on samples from the same source and if they were examined under identical experimental conditions.

Previous Work

The many studies of the mechanism of aging in duralumin have been more or less crystallized by a series of papers by Fink and Smith[1,2,3] and a recent paper by Cohen.[4] The former authors believe that a simple precipitation theory is adequate to account for the various phenomena

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These experiments represent a portion of a thesis presented by R. W. Lindsay in partial requirement for the degree of Doctor of Science at M. I. T. Manuscript received at the office of the Institute July 5, 1938; revised Jan. 4, 1939. Issued as T.P. 1064 in Metals Technology, April, 1939.

* Association of Manufacturers of Chilled Car Wheels, Chicago, Ill.

† Associate Professor of Physics of Metals, Department of Metallurgy, Massachusetts Institute of Technology.

[1] References are at the end of the paper.

observed. According to this view, one would conclude that the distortion of the crystal lattice is an accompaniment of the incipient precipitation. On the other hand, Cohen feels that the lattice distortion represents a distinct stage in the process of aging, which precedes or prepares the way for the precipitation. These authors agree on the experimental evidence but differ in interpretation. In this connection, the effect of lattice distortion introduced by mechanical deformation might throw additional light on the problem.

As to the effects of the cold-working on the mechanical properties of duralumin, there are two important papers, one by Fraenkel[5] and one by Teed.[6] These aging experiments were conducted at room temperature. Other pertinent studies have been made by Burns,[7] Watase,[8] Bollenrath,[9] Bachmetew[10] and Meissner.[11] A review of their work indicates a general agreement on the following points:

1. Cold-work after the solution heat-treatment results in a sudden increase in hardness, the value approaching that obtained by aging.

2. The cold-worked samples show no incubation period at the beginning of aging.

3. The greater the amount of cold-work, the quicker will the hardness and strength reach the maximum value.

4. Cold-work after aging also results in an increase of strength and hardness, and the maximum values of these properties of which the alloy is capable are obtained by this treatment.

Experimental Procedure

In the present investigation the experimental work consisted of a careful comparison of the behavior of a single alloy aged in the normal fashion, aged after cold-working and cold-worked after normal aging. Aging was carried out at four different temperatures. The tools used for the investigation were hardness, electrical resistivity and X-ray diffraction measurements.

The alloy used was a commercial duralumin, which gave the following typical analysis: copper, 3.98 per cent; magnesium, 0.82; manganese, 0.51; silicon, 0.22; iron, 0.70; aluminum, remainder.

The samples were given a solution heat-treatment at 515° C. for 1 hr. and quenched into tap water. The alloys were then either simply aged, deformed and aged, or aged and deformed and their behavior studied by the methods mentioned previously. The samples were aged in constant-temperature baths at 25°, 100°, 190°, and 300° C., the aging time being cumulative and a maximum time of one week being employed at each temperature. Samples were removed from the aging baths after definite intervals, measured at 25° and then returned to the bath.

Deformation of the samples was accomplished by drawing through

a draw plate. The degrees of deformation, indicated in terms of reduction of area, were obtained by taking the alloy as received in the form of a ½-in. diameter rod, turning it to different initial diameters and drawing to the same final diameter. The smaller reductions were obtained in one pass, while two passes were required for the higher reductions.

Hardness measurements (Rockwell F scale) were made on the surface of the round samples (varying from 0.141 to 0.125-in. radius) for the sake of rapidity and to avoid further extraneous deformation of the samples. Although such measurements give hardness values lower than those obtained on flat surfaces, they were comparable throughout the course of the investigation. Values reported are averages of at least three readings. The hardness results were reproducible within ± 2 points.

Lattice-parameter measurements were made on the same type of surface as the hardness measurements, using the familiar back-reflection method, with a modified method of holding the sample. The sample was rotated and moved laterally by hand during the exposure. Diffraction from the (511) and (333) families of planes, using copper radiation, yielded the lines from which lattice-parameter calculations were made. Where the lines were broad, the parameter range has been indicated by a shaded band rather than a sharp line. Where the lines are sharp, the probable error is about ± 0.0002 Å., but this value increases as the lines become broader.

Reductions of area of 5 per cent and 22 per cent were given to the samples on which hardness and lattice-parameter measurements were made.

Changes in electrical resistivity were measured on samples of 0.114 to 0.100-in. diameter, using a Kelvin double bridge. The reproducibility on the undeformed samples was of the order of magnitude of 0.3 per cent, but the precision was somewhat less in the deformed samples, owing to experimental difficulties in the deforming operation. The changes in resistivity are expressed as percentage changes. Since deformation of these samples was carried out in another section of the draw plate, the reductions of area obtained (8 and 23 per cent) were not quite the same as with the samples for hardness and X-ray measurements.

Experimental Results

It was decided to present the results for the most part in the form of graphs (Figs. 1 to 4) for the sake of brevity. Actual experimental values are available in the original research.[12] The graphs are plotted for undeformed samples and samples given the maximum reduction of area of about 23 per cent. It should be mentioned that the results for the lower reduction of area are consistent with those shown in the graphs.

Discussion of Results

A consideration of the hardness curves would indicate that the normal aging process involves three overlapping stages. At 25° C. the aging process apparently involves lattice distortion as shown by the increases in hardness and resistivity (Fig. 1). There is no change in either the position or breadth of the X-ray diffraction lines. At 100° C., this

Table 1.—*Comparison of Stable and Unstable Samples of Same Hardness*

Reduction of Area, Per Cent	Hardness Change, Rockwell F		Resistivity Change, Per Cent		Parameter Change, Å.		Line Breadth Condition of Alpha Doublet	
	Stable[a]	Unstable	Stable	Unstable	Stable	Unstable	Stable	Unstable
5	+5	+18			−0.004	−0.005	Barely resolved	Unresolved
8			+2.4	+2.5				
22	+11	+23			−0.004	−0.007	Barely resolved	Unresolved
23			+2.5	+3.8				

[a] Stable samples prepared by aging for one hour at 300° C.

Table 2.—*Hardness Changes in Sample Aged One Week, Reduced 23 Per Cent in Area and Reaged*

Aging Time	Hardness, Rockwell F	Aging Time	Hardness, Rockwell F
Aging Temperature, 25° C.			
As aged	91	88 hours	97
Worked	98	112	97
40 hours	96	136	97½
64	97	160	98
Aging Temperature, 190° C.			
As aged	81½	38 hours	71
Worked	75	62	72
14 hours	73	86	71

lattice-distortion stage is followed by the beginning of a second stage (Fig. 2). Hardness shows a second increase and resistivity exhibits a slight decrease. The behavior of the lattice parameter is the same as at 25°. At 190° C. the three stages of the process are clearly evident (Fig. 3). The first two stages are indicated in a manner similar to that at

100°; namely, two hardness steps and an increase, followed by a gradual decrease in resistivity. The third stage is definitely one involving general precipitation. Its indications are a third hardness step concurrent with decreasing resistivity and increasing lattice parameter. At 300° C. the process proceeds so rapidly that the effects of general precipitation obscure the first and second stages (Fig. 4). This postulation of the aging process in duralumin has already been discussed by Cohen[4] on the basis of more detailed evidence.

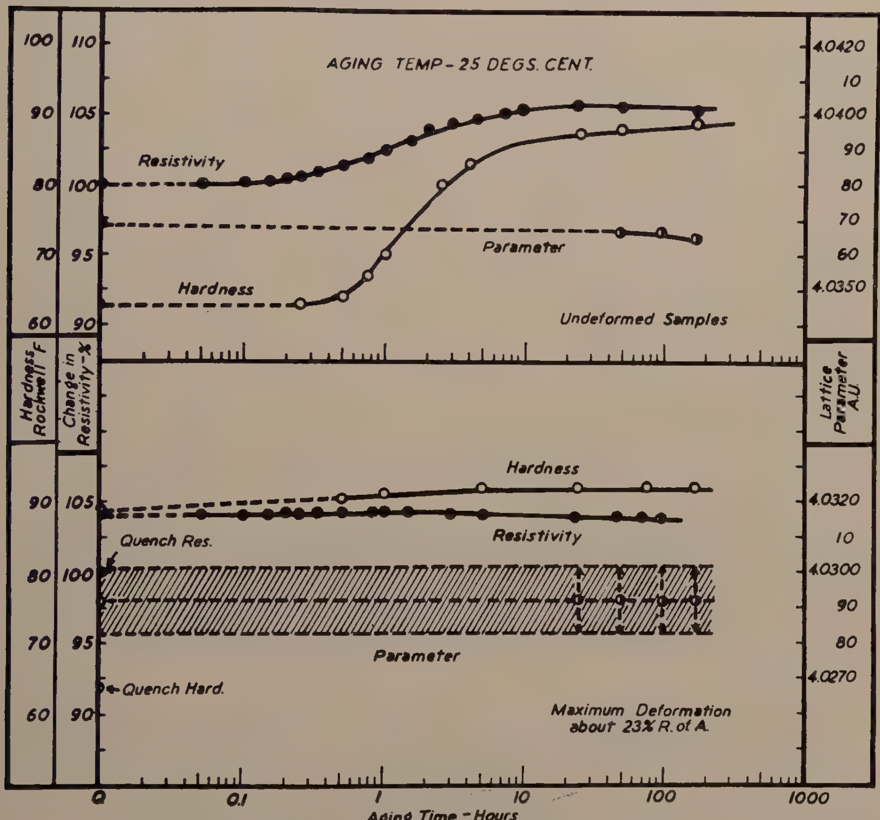

FIG. 1.—CHANGES IN HARDNESS, ELECTRICAL RESISTIVITY AND LATTICE PARAMETER DURING AGING AT 25° C. OF UNDEFORMED AND DEFORMED SAMPLES.

The first stage of aging involving lattice distortion is of particular interest in this work. Distortion of the lattice can also be produced by mechanical deformation. The effects produced in this manner are in the same direction as those arising from lattice distortion during aging; namely, increases in hardness and resistivity. On this basis it would be expected that a mechanical distortion might accomplish what is accomplished by spontaneous distortion of the lattice during aging at 25°. The experimental evidence shows that this occurred (Fig. 1). Increasing

deformation approximates the distortion produced by aging, leaving less and less to be accomplished by subsequently aging the deformed samples. The conclusion is that mechanical distortion of the quenched samples approximates the lattice distortion that can be accomplished by aging alone. It must be admitted that although the two distortions are apparently essentially similar, they are not identical. Mechanical dis-

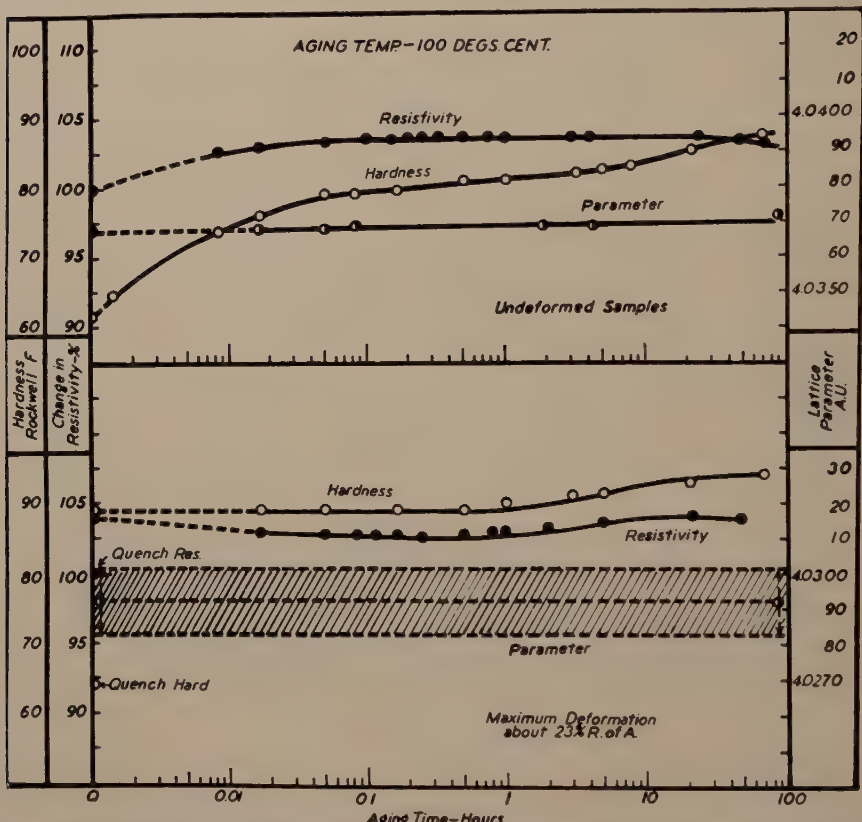

FIG. 2.—CHANGES IN HARDNESS, ELECTRICAL RESISTIVITY AND LATTICE PARAMETER DURING AGING AT 100° C. OF UNDEFORMED AND DEFORMED SAMPLES.

tortion causes broadening of the diffraction lines but distortion of the lattice resulting from aging does not. This might be attributed to differences in the distribution of the strains in the two instances. As a result of the former, strains are more or less uniformly distributed while the strains set up by aging are localized. Such a localized strain condition has little effect on the diffraction lines compared to the large unstrained area, and the lines remain sharp. On the other hand, mechanical distortion produces strains throughout the grain and consequently the diffraction lines broaden.

One cannot decide from the evidence whether deformation causes incipient precipitation. A comparison was made on stable and unstable samples of the same hardness ($60–62R_F$) with the belief that deformation might cause localized precipitation in the unstable samples. In the latter greater hardness and resistivity increases were noted as well as increased breadth of lines (Table 1). It is generally believed that plastic

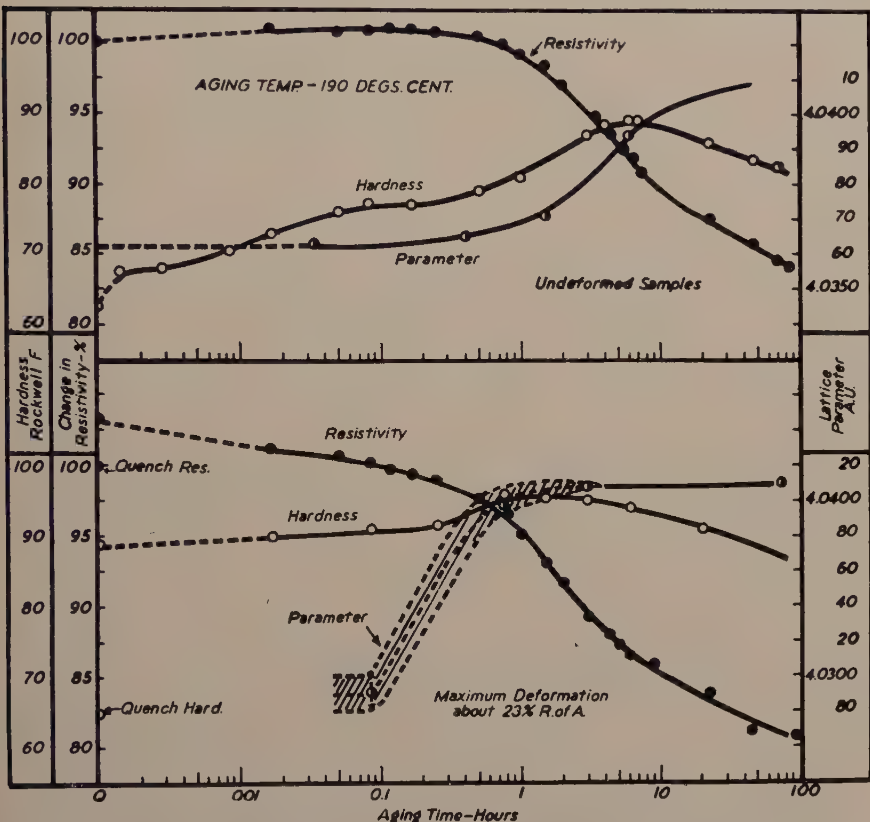

FIG. 3.—CHANGES IN HARDNESS, ELECTRICAL RESISTIVITY AND LATTICE PARAMETER DURING AGING AT 190° C. OF UNDEFORMED AND DEFORMED SAMPLES.

deformation will cause localized precipitation and some of the results here appear to indicate that this is so. Thus, the lines broaden more in deformed unstable samples than they do in deformed stable samples. Furthermore, the maximum resistivity attained in deformed and aged samples is less than that attained in normally aged samples (Fig. 1). Both these points would be in support of the thought that localized precipitation does occur, but are not necessarily definite proof. It may be that the differences are solely due to differences in the strain-hardening characteristics of stable and unstable samples.

It is known that samples aged initially at 25° at first soften when reaged at higher temperatures; for instance, 100° or 200°. It would be expected that samples deformed after quenching would behave similarly. This is not true, as may be seen from Figs. 2 and 3. This is another indication that mechanical distortion of the lattice and distortion arising from aging are not identical. It may be, however, that earlier occur-

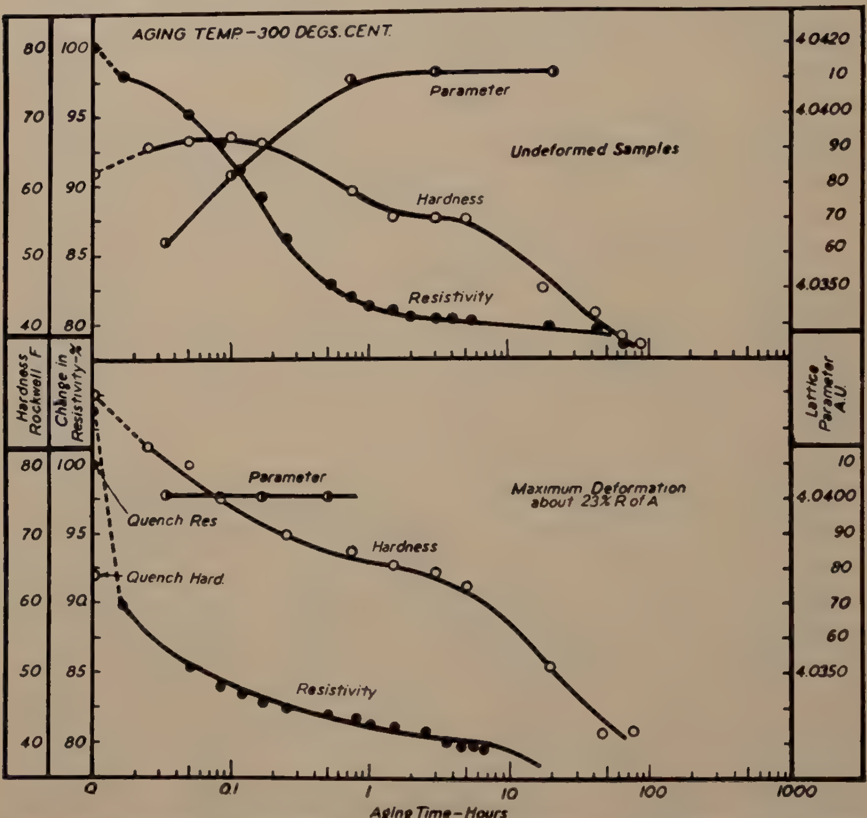

FIG. 4.—CHANGES IN HARDNESS, ELECTRICAL RESISTIVITY AND LATTICE PARAMETER DURING AGING AT 300° C. OF UNDEFORMED AND DEFORMED SAMPLES.

rence of the second stage of aging in the worked samples offsets the expected softening.

It is apparent that the third stage, general precipitation, is neither accomplished nor prevented by deformation. This stage is still apparent at those temperatures at which it occurs in the normal aging process. However, it does occur more rapidly, as shown by the property changes at 190° and 300° (Figs. 3 and 4).

Some ambiguity is apparent in the X-ray results. In the first place, the lattice parameter of the deformed samples is smaller than that of the quenched samples, which would indicate that more copper has been

put into solution by deformation, but this is hardly likely. Rather, it is probably the result of a change in stress during working. On the other hand, when aging involved general precipitation the lattice parameter was larger than that for pure aluminum, which was used as a standard in the X-ray work. Since this was true in both undeformed and deformed samples, the difference is apparently a question of composition rather than stresses.

Experimental results show that deforming samples previously aged one week at 25° and 100° results in a simple mechanical distortion of the lattice; in other words, strain-hardening. Tables 2 and 3 are typical of the behavior of hardness at 25° and 190°. Slight decreases in resistivity on reaging at these temperatures are apparently caused by relief of stress.

Deformation of samples aged at 190° resulted in softening rather than hardening. Electrical resistivity showed a slight increase and diffraction lines broadened considerably. This softening may be the result of deformation causing a redistribution of strains existing in the aged samples, thus yielding an apparently lower indentation hardness.

Conclusions

The following conclusions may be drawn from this investigation:

1. Mechanical distortion of quenched samples is essentially similar to the spontaneous distortion of the lattice produced by aging at 25° C.
2. Mechanical distortion and spontaneous distortion are, however, not identical, since the former results in broadening of the X-ray diffraction lines and the latter does not.
3. The evidence suggests some amount of incipient precipitation as a result of deformation, but is not too definite.
4. General precipitation takes place in deformed samples at the same temperatures and in the same manner as it does in undeformed samples.
5. Deformation of aged samples has for its results a simple strain-hardening.

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DISCUSSION

M. L. V. Gayler,* Teddington, Middlesex, England (written discussion).—I have been investigating the effect of cold-work on the aging of a 4 per cent copper-aluminum alloy of high purity, and I have obtained some results which, I think, throw light on one or two points raised by the authors.

On page 118 they remark: "It is known that samples aged initially at 25° at first soften when reaged at higher temperatures; for instance 100° and 200°. It would be expected that samples deformed after quenching would behave similarly. This is not true, as may be seen in Figs. 2 and 3. This is another indication that mechanical distortion of the lattice and distortion arising from aging are not identical. It may

Fig. 5.—Cold-forged 1-inch chill, 4 per cent copper-aluminum alloy.
Heat-treated 2 hr. at 530° C., quenched in water at room temperature and cold-rolled from 5⁄16 to 3⁄16 inch. Etched with 25 per cent nitric acid in water at 70° C. × 150.

be, however, that earlier occurrence of the second stage of aging in the worked samples offsets the expected softening."

The following experimental data support the authors' views: A cold-forged 1-in. chill of 4 per cent copper-aluminum alloy of high purity was heat-treated 2 hr. at 530° C., quenched in water at room temperature and immediately cold-rolled from a thickness of 5⁄16 to 3⁄16 in. Brinell-hardness measurements taken over a period of five days showed that no further aging took place during that time: the hardness immediately after quenching being 95, which is approximately the maximum attained during room-temperature aging. The microstructure of the cold-worked alloy etched with 25 per cent HNO_3 in water at 70° C. is shown in Fig. 5 under a magnification of 150 diameters. Apart from the varied staining of the grains, which, however, may be significant, the structure is typical of a cold-worked material: no visible precipitation was observed.

If the alloy be heat-treated at 200° C. marked changes occur both in hardness and microstructure. Fig. 6 represents the hardness-time curve and shows that the initial effect of heat-treating the cold-rolled material is to cause an immediate increase in hardness. This rises to a maximum hardness of 102 Brinell in about 55 min., after which the alloy rapidly softens. In comparison, the hardness of the alloy quenched

* Metallurgy Department, National Physical Laboratory.

normally and then aged at 200° C. immediately, rises to a maximum hardness of 100 Brinell in about 8 hr., after which softening sets in.

The microstructure of the cold-worked alloy aged at 200° C. has been examined after various time intervals. After each heat-treatment the specimens were polished and etched with 25 per cent HNO_3 in water at 70° C. Figs. 7 and 8, under a magnification of 150 diameters, show the characteristic "strain" figures, which were developed by etching specimens aged ¼ and 1 hr. at 200° C., respectively. The lines and darkened regions increase in degree as the time of aging is prolonged (cf. Figs. 7 and 8).

If the microstructures are examined under a magnification of 2000 diameters, the "strain" lines resolve themselves and are seen to be a very fine precipitate. Fig. 8 is a typical area of the alloy aged ¼ hr. at 200° C., showing "strain" lines crossing each other. The structure of the alloy aged 120 hr. is given in Fig. 10 under a magnification of 2000 diameters, and this shows that a much more pronounced precipitation has taken place, again in the form of very fine rounded particles.

The nature of this precipitate is uncertain, but it is probably, in the early stages of aging, the intermediate phase of Wassermann and Weerts,[13] since an X-ray analysis of the polished and etched surface of a specimen aged one day at 200° C. showed evidence of a phase other than $CuAl_2$.

It is therefore improbable that $CuAl_2$ is present in alloys aged at 200° C. for periods less than one day; therefore the precipitates seen in Figs. 7 to 9 are probably the intermediate phase. After aging for 120 hr., some of the fine precipitated phase may

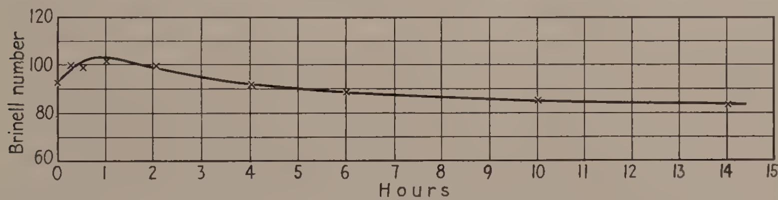

Fig. 6.—Hardness-time curve of alloy in Fig. 5. Heat-treatment at 200° C.

still be this phase; $CuAl_2$, however, is present in the grain boundaries, since the particles in them are stained black by the etching reagent.

Reference should be made to the results of Bosshard and Hug,[14] whose researches on "strain" figures in aluminum alloys of other compositions were published just after I had observed the facts described. These investigators did not, however, identify precipitation in the "strain" figures until after prolonged aging.

The experimental facts which I have just put forward show why no softening should be expected when cold-rolled material is aged at higher temperatures: they support the authors' suggestion that the "earlier occurrence of the second stage of aging in the worked samples offsets the expected softening." It is obvious that the second stage of the aging process sets in at an accelerated rate when aging is carried out on cold-worked material at high temperatures. It is probable, as the authors suggest, that "some amount of incipient precipitation as a result of deformation" is present. There is no microscopic evidence to support this view but an "incipient" precipitation is unlikely to be detected by this method of analysis. Calvet, Jacquet and Guinier[15] and Preston[16] have shown that plates of copper atoms are formed during room-temperature aging,

[13] G. Wassermann and G. Weerts. *Metallwirtschaft* (1935) **14**, 605.

[14] M. Bosshard and H. Hug: *Schweiz. Archiv* (1938) **4**, (5), 127; *Metallwirtschaft* (1938) **17**, (26), 708.

[15] J. Calvet, P. Jacquet and A. Guinier: *Compt. rend.* (1938) **206**, 1972.

[16] G. D. Preston: *Proc.* Roy. Soc. (1938) **A-167**, 526.

and that these increase in size and number as aging proceeds, and that at higher aging temperatures the intermediate phase appears at the expense of the former.

In the cold-worked copper-aluminum alloy, it appears from hardness measurements that the alloy is in the fully aged state. It is possible, therefore, that the plates

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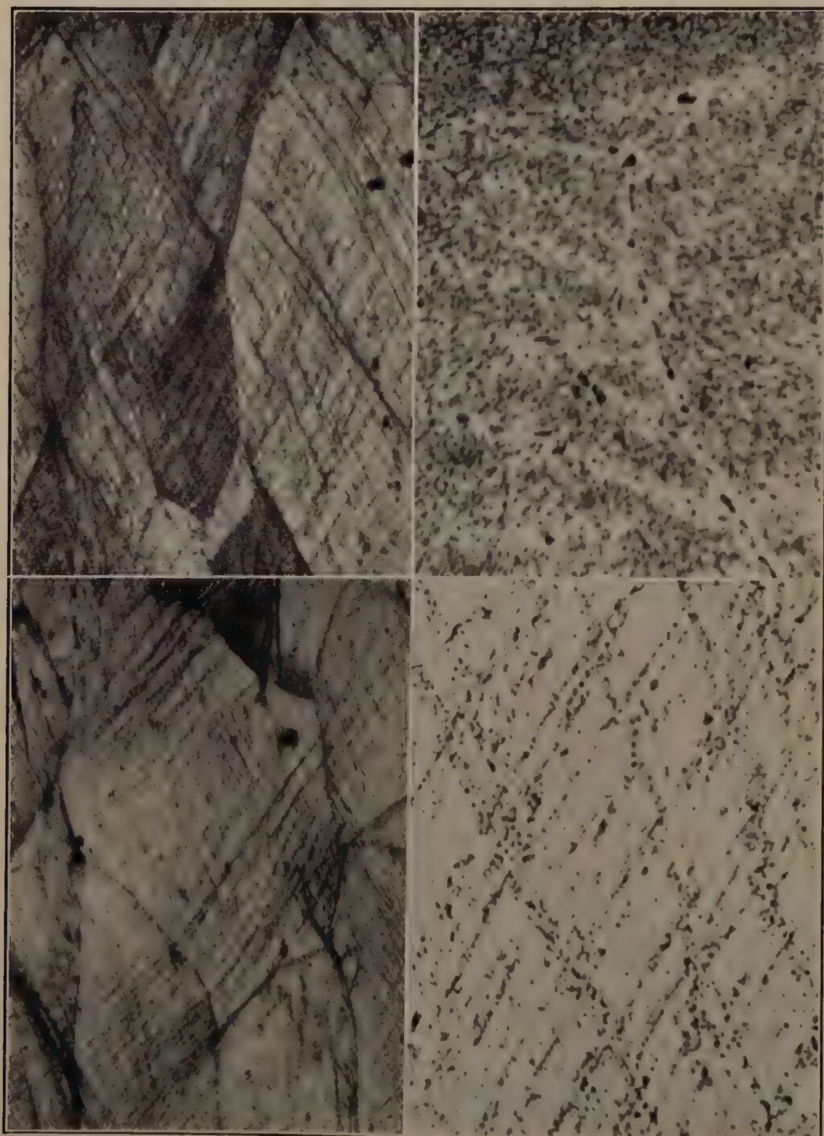

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FIGS. 7 AND 8.—SAME ALLOY AS FIG. 5.
Strain figures developed by etching 1/4 and 1 hour, respectively, at 200° C. × 150.
FIGS. 9 AND 10.—FINE PRECIPITATE IN SAME ALLOY. × 2000.

of copper atoms formed by the accelerated aging due to cold-work are too large for re-solution at higher aging temperatures. Hence the intermediate is formed immediately on aging at higher temperatures. The fact that the hardness increased imme-

diately on aging the cold-worked alloy at temperatures of 130°, 150° and 200° C. supports this deduction.

R. W. Lindsay and J. T. Norton (written discussion).—It is gratifying to learn that Dr. Gayler's findings are in accord with ours. Although the behaviors of Dr. Gayler's alloy and of that used in this investigation differ somewhat in response to aging at 200° C. after cold-work, both show an increase in hardness immediately upon aging at this temperature. The differences that do exist between the two are quite probably the result of differences in purity of the alloy, that used in our investigation being a commercial duralumin. Whereas Dr. Gayler found an initial hardening followed by softening at 200°, we found an initial gradual hardening followed by a more pronounced hardening and finally a softening.

Dr. Gayler's microscopic work indicates that the initial hardening is due to a precipitation of an intermediate phase. Although no microscopic work was done in our investigation, the behavior of electrical resistivity appears to offer confirmatory evidence. Dr. Gayler attributes the initial hardening to accelerated aging, which produces plates of copper atoms of such a size that re-solution (which is considered responsible for the softening occurring when a fully aged alloy is re-aged at 200°) is prevented and the intermediate phase immediately forms. The inference is then that formation of this intermediate phase takes place by slightly differing mechanisms in normally aged alloys and in alloys cold-worked and then aged, since the re-solution state is postulated to be prevented in the latter instance. The other possibility is that incipient precipitation is actually initiated by the cold-working operation. Naturally, both ideas are rather speculative in nature but are logical postulations from the evidence at hand.

Some Aspects of the Recrystallization of Cold-worked Aluminum and Aluminum Alloys

By L. W. Eastwood,* Member A.I.M.E., R. W. James,† Junior Member, and R. F. Bell‡

(New York Meeting, February, 1939)

Part 1. Effect of Heating Rate upon Recrystallized Grain Size of Aluminum and Aluminum Alloys

Among those concerned with the annealing and heat-treating of aluminum and aluminum alloys, it is well known that after cold-working a coarser grain is usually produced by slow heating than by more rapid heating. Consequently, for the control of the grain size produced by annealing or heat-treating cold-worked aluminum and aluminum alloys, the heating rate is of considerable practical importance. References in the current literature on the effect of heating rate are numerous, but it appears neither necessary nor desirable to give here a review of the former work done on this subject.

It became evident during some preliminary work on the recrystallization of aluminum and aluminum alloys that the effect of heating rate depended upon the type of microstructure of the metal. This observation led to the following study of the relationship of the type of microstructure of the alloy to the effect of the heating rate.

Materials Investigated

Analyses of the aluminum and aluminum alloys investigated are given in Table 1. Three classes of material are listed, as follows:

Class I.—Belonging to the first class are pure aluminum and aluminum containing a second constituent that is soluble in the aluminum matrix at

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This paper is based upon theses submitted to the faculty of the Case School of Applied Science, Cleveland, Ohio, by R. W. James in partial fulfillment of the requirements for a Master of Science degree in metallurgy, and by R. F. Bell in partial fulfillment of the requirements for a Bachelor of Science degree in metallurgy. Manuscript received at the office of the Institute Dec. 1, 1939. Issued as T.P. 1048 in Metals Technology, February, 1939.

* Research Metallurgist, Aluminum Company of America, Cleveland, Ohio.

† Research Metallurgist, Aluminum Company of America, and graduate student, Case School of Applied Science, Cleveland, Ohio.

‡ Assistant Metallurgist, Aluminum Company of America, Cleveland, Ohio.

all temperatures between room temperature and the solidus line. This structural class consists of a single phase throughout the range from room temperature to the heat-treating temperature.

Class II.—The alloys of class II are characterized by the presence of a second constituent in the aluminum matrix, the second constituent having only limited solubility at room temperature but considerable solubility at high temperatures. The quantity of the second constituent is just sufficient to enable complete solution in the aluminum matrix at temperatures near the solidus line. These alloys consist of a single phase at high temperatures and two phases at lower temperatures.

Class III.—This class of alloys is characterized by the presence of a second phase that is essentially insoluble at all temperatures between room temperature and the solidus line. These alloys consist of an aggregate throughout the solid state.

TABLE 1.—*Chemical Compositions of Alloys*

Class	Composition, Per Cent				
	Alloy	Cu	Fe	Si	Others
I	99.95 Al	0.01	0.02	0.01	
I	Al + 2 Zn	0.01	0.01	0.01	2.33 Zn
I	Al + 2 Mg	0.01	0.03	0.02	2.03 Mg
II	Al + 4 Cu	4.20	0.04	0.01	
II	Al + 1 Mg_2Si	0.01	0.02	0.37	0.76 Mg
II	Al + 0.5 Si	0.01	0.02	0.45	
II	Al + 8 Mg	0.01	0.02	0.02	8.04 Mg
III	Al + 1.5 Fe + 0.75 Si	0.01	1.59	0.73	
III	Al + 3 Mn	0.01	0.07	0.03	2.74 Mn
III	Al + 0.3 Ti	0.06	0.14	0.17	0.34 Ti
III	99.3 Al	0.01	0.41	0.27	
II and III	Duralumin	4.14	0.57	0.20	0.43 Mg 0.44 Mn

Experimental Procedure

The materials were prepared from ingots measuring 3½ by 3½ by 12 in. The ingots were scalped, preheated, and then hot-forged to bars ¾ by ¾ in. The ¾-in. bars were cold-rolled with intermediate anneals to the desired thickness. They were then annealed 16 hr. at 650° F. and cooled slowly in the furnace to precipitate soluble constituents. Following this anneal, they were cold-rolled to give reductions in thickness of 2 per cent, 5 per cent, 10 per cent, 30 per cent and 75 per cent in each. The final reductions produced strips 0.04 in. thick.

Specimens of each of these types of cold-worked strips were then heated at two temperatures, one lot being treated at 750° F. and the

second lot at 950° F. Three heating rates were utilized for each of the temperatures. Slow, medium and fast heating rates were effected as follows:

The slow heating rate was obtained by placing the specimens in the cold furnace and heating them up with the furnace; 45 min. was required to reach 750° F. and 75 min. to reach 950° F. The specimens were held at temperature for 30 min., then quenched in cold water to preserve the structure existing at the end of the thermal treatment.

The medium heating rate was accomplished by placing the specimens in the furnace after it had reached the desired temperature. The specimens were held 30 min. and quenched in cold water.

The rapid heating rate was effected by plunging the specimens into a fused salt bath previously heated in the furnace to the desired temperature. A salt-load weight ratio of 36:1 was utilized. To compensate for the slight drop in temperature of the bath, the fused salt was heated to 760° F. for the 750° F. anneal and to 965° F. for the 950° F. treatment. The samples were held in the salt bath for 30 min. and quenched in cold water.

Thus, in this work, twelve different materials were reduced five different degrees by cold-rolling, after which similar specimens were heated at three different heating rates to two different temperatures. Subsurfaces parallel to the rolling plane and near the center of the strips were polished and grain counts made. On two of the alloys it was difficult to make a grain count because they were fine-grained and contained a considerable amount of insoluble constituent. The relative grain size of these alloys was determined by means of X-ray diffraction patterns.

Discussion of Results

In this paper the replacement of the strained material by unstrained grains, as observed by X-ray diffraction or microscopic means, is called "recrystallization" and the absorption of one unstrained grain by another after recrystallization is complete is called "coalescence." This definition of recrystallization covers the process of the formation of new grains from the original nucleus to the completed grain. On the basis of volume, most of this growth can be observed by means of a microscope, the initial stages of the nucleus growth being, however, well advanced by the time the new grains are visible at high magnification. When such new grains collectively just occupy the entire volume of the specimen or portion of the specimen, recrystallization of this portion is considered complete. Further grain growth occurs by coalescence. Throughout this paper the term "recrystallized grain size" will refer to the final grain size produced by any thermal treatment that permitted recrystallization to occur. In many instances the term will refer to structures that represent considerable coalescence subsequent to actual recrystallization.

Considerable change must occur in the atomic structure and in the positions of the atoms before new grains are visible. The observation of these changes is restricted, of course, by the limitations of present experimental methods. The processes that precede the formation of new grains are collectively designated as "recovery."

These definitions are necessarily arbitrary, but they form the initial and essential basis for any discussion of this subject. If and when greater knowledge of the processes involved is at hand, recrystallization might well be considered to occur in the stage now designated as recovery.

TABLE 2.—*Average Number of Grains per Square Millimeter, Class I, Single-phase Materials*

Composition, Per Cent	Reduction, Per Cent	Grain Size before Last Cold-rolling	Heated to 750° F.			Heated to 950° F.		
			Slow Heating Rate	Medium Heating Rate	Fast Heating Rate	Slow Heating Rate	Medium Heating Rate	Fast Heating Rate
99.95 Al	2	121	121[a]	121[a]	121[a]	2	2	4
	5		16	16	16	4	4	4
	10		25	25	25	4	6	4
	30		36	36	36	4	9	4
	75		25	25	25	4	6	2
Al + 2 Zn	2	144	144[a]	144[a]	144[a]	½	½	½
	5		½–144[b]	144[a]	144[a]	½	½	½
	10		4	4	9	2	2	2
	30		16	16	16	2	2	2
	75		16	16	16	2	2	2
Al + 2 Mg	2	225	225[a]	225[a]	225[a]	2	2	5
	5		9–64	16	16	4	7	7
	10		64	64	64	9	9	9
	30		100	100	100	9	9	9
	75		196	196	169	7	7	9

[a] Not recrystallized.
[b] Partially recrystallized; all others completely recrystallized.

The data on alloy classes I, II and III and on the two commercial products, 99.3 per cent aluminum and duralumin, are shown in Tables 2, 3, 4 and 5, respectively. The data in the tables indicate the specimens that are recrystallized, partly recrystallized, or not recrystallized, these conditions having been identified in the following manner. The original materials are relatively fine grained while, as is well known, the recrystallized grains are coarse at the low degrees of cold deformation. From examination of the data, it is apparent that, at the low reductions, a considerable grain coarsening accompanied recrystallization. Assuming, then, that the relatively coarse-grained low-reduction samples have recrystallized, the same material cold-worked to higher degrees and

subjected to the same thermal treatment would, of course, have recrystallized also. To check this criterion for distinguishing between recrystallized and unrecrystallized materials, diffraction patterns were made of some specimens. It was found that the well-known patterns indicative of cold-worked materials were produced when the grain size of the treated specimens was the same as the grain size before the last cold-working

TABLE 3.—*Average Number of Grains per Square Millimeter, Class II, Alloys Containing Second Phase Completely Soluble at Temperature near Solidus*

Composition, Per Cent	Reduction, Per Cent	Grain Size before Last Cold-rolling	Heated to 750° F.			Heated to 950° F.		
			Slow Heating Rate	Medium Heating Rate	Fast Heating Rate	Slow Heating Rate	Medium Heating Rate	Fast Heating Rate
Al + 4 Cu.......	2	4000	4000[a]	4000[a]	4000[a]	9	16	16
	5		1	145	145	16	16	16
	10		4	210	325	16	16	16
	30		225	785	1150	25	25	25
	75		1025	2304	2704	25	25	25
Al + 1 Mg_2Si....	2	550	550[a]	550[a]	550[a]	2	4	3
	5		550[a]	550[a]	550[a]	5	8	6
	10		5	16	25	8	8	10
	30		30	40	145	12	14	8
	75		75	195	250	6	15	4
Al + 0.5 Si......	2	325	325[a]	325[a]	325[a]	1	1	2
	5		1	½	1	1	2	5
	10		36	49	64	3	4	9
	30		49	64	64	4	5	9
	75		81	121	100	8	8	8
Al + 8 Mg......	2	225	225[a]	225[a]	225[a]	7	6	7
	5		4–225[b]	225[a]	4–225[b]	7	12	10
	10		16	25	100	12	12	12
	30		64	100	144	25	20	25
	75		64	100	64	7	12	9

[a] Not recrystallized.

[b] Partially recrystallized; all others completely recrystallized.

operation. When the coarsening in grain size occurred, the diffraction pattern indicated the formation of new unstrained—i.e., recrystallized—grains.

The data in the four tables are fairly consistent. As might be expected, when a coarse grain exists, there is more variation in the average grain size because the fewer number of grains present permits a wider variation in average results.

The data in Table 2 indicate that, with the single-phase materials, for a given reduction and heating temperature, no variation in the recrystal-

lized grain size is produced by differences in heating rate. Considerable coalescence has occurred in all the specimens heated to 950° F. and in the specimens that are given considerable reductions and annealed at 750° F.

In Table 3 the copper and the magnesium silicide alloys reduced a given amount and heated at 750° F. show an orderly decrease in recrystallized grain size with increased heating rates. After the 750° F. treatment, both of these alloys contained numerous undissolved particles of the

TABLE 4.—*Average Number of Grains per Square Millimeter, Class III, Alloys Containing Second Phase Practically Insoluble at All Temperatures below Solidus*

Composition, Per Cent	Reduction, Per Cent	Grain Size before Last Cold-rolling	Heated to 750° F.			Heated to 950° F.		
			Slow Heating Rate	Medium Heating Rate	Fast Heating Rate	Slow Heating Rate	Medium Heating Rate	Fast Heating Rate
Al + 1.5 Fe + 0.75 Si.	2	4625	4625[a]	4625[a]	4625[a]	4625[a]	4625[a]	4625[a]
	5		4625[a]	4625[a]	4625[a]	4625[a]	4625[a]	4625[a]
	10		4625[a]	4625[a]	4625[a]	16	36	64
	30		144	256	400	400	576	784
	75		1024	1296	1936	1296	1600	3136
Al + 3 Mn........	2	U[c]	U[a]	U[a]	U[a]	U[a]	U[a]	U[a]
	5	(From X-	U[a]	U[a]	U[a]	U[a]	U[a]	U[b]
	10	ray diffrac-	U[a]	U[a]	U[b]	A	B	C
	30	tion pat-	A	B	C	D	E	F
	75	terns)	D	E	F	G	H	J
Al + 0.3 Ti........	2	U[c]	U[a]	U[a]	U[a]	U[a]	U[a]	U[a]
	5	(From X-	U[a]	U[a]	U[a]	U[a]	U[a]	U[b]
	10	ray diffrac-	U[a]	U[a]	U[b]	A	B	C
	30	tion pat-	A	B	C	D	E	F
	75	terns)	D	E	F	G	H	J

[a] Not recrystallized.

[b] Partially recrystallized.

[c] U represents unrecrystallized material; A represents the largest recrystallized grain size and J the smallest recrystallized grain size. The series A to J represents the relative grain sizes shown but only for a given material heated to the specific temperature indicated.

soluble phase. The data for the silicon and magnesium alloys heated to 750° F. show some evidence of the effect of heating rate, but the effect is not so pronounced as in the first two materials. The lesser effect is probably explained by the almost complete solution of the soluble phases in these two alloys at 750° F. All of the materials in Table 3 show little or no effect of heating rate when treated at 950° F. A complete solution of the soluble phases at this temperature has apparently permitted class II alloys to assume a final grain size independent of heating rate. It is probable that the recrystallization of the alloys precedes the solution of

the soluble phase. If so, just after complete recrystallization, the grain size of class II alloys cold-worked and heated to 950° F. must have been finest in the rapidly heated specimens. This difference in grain size apparently has been eliminated by subsequent coalescence. This is substantiated by the fact that, for a given heating rate, the final grain size is approximately similar in specimens given different degrees of reduction, though the grain size just after complete recrystallization of the specimens reduced 2 per cent must have been markedly larger than those in the specimens reduced 75 per cent. This difference in grain size, too, has been largely though not completely eliminated by subsequent coales-

TABLE 5.—*Average Number of Grains per Square Millimeter, Commercial Alloys*

Composition, Per Cent	Reduction, Per Cent	Grain Size before Last Cold-rolling	Heated to 750° F.			Heated to 950° F.		
			Slow Heating Rate	Medium Heating Rate	Fast Heating Rate	Slow Heating Rate	Medium Heating Rate	Fast Heating Rate
99.3 Al[b].........	2	1930	1930[a]	1930[a]	1930[a]	1930[a]	1930[a]	1930[a]
	5		1930[a]	1930[a]	1930[a]	1930[a]	1930[a]	1930[a]
	10		1930[a]	1930[a]	1930[a]	1/8" dia.	4	4
	30		25	64	121	100	144	196
	75		256	400	784	484	900	1930
Duralumin[c]......	2	8450	8450[a]	8450[a]	8450[a]	8450[a]	8450[a]	8450[a]
	5		8450[a]	8450[a]	8450[a]	8450[a]	8450[a]	8450[a]
	10		8450[a]	8450[a]	8450[a]	16	36	40
	30		64	144	400	144	600	1024
	75		1024	2304	5184	1932	2700	5766

[a] Not recrystallized; all others completely recrystallized.
[b] Class III.
[c] Combination of class II and class III.

cence at 950° F. Coalescence is greatly facilitated by the absence of a second phase finely dispersed in the aluminum matrix. Consequently, considerable coalescence has occurred at 950° F. in all the alloys of this class, and only slight coalescence has occurred at 750° F. if a substantial amount of undissolved second phase remains.

The data of Table 4 show a distinct effect of heating rate in class III alloys (those containing insolubles at all temperatures below the solidus) at both temperatures and for all reductions at which recrystallization occurred. The commercial alloys shown in Table 5 display a similar effect. Both of these commercial materials, of course, contain considerable amounts of insoluble constituent at all temperatures below the solidus.

The collective data show that, if a second phase remains after the thermal treatment, a coarser grain is obtained by slow heating than is

obtained by rapid heating. If the second phase is of such a nature that it is completely dissolved during the time at the heating temperature, it has little or no effect on the final grain size, provided the time after solution of the soluble phase is sufficient to permit considerable coalescence.

It is quite evident, then, that a second microstructural phase must be present if the grain size produced by a rapid rate of heating is finer than that obtained by a slower rate of heating. The explanation for this phenomenon is not clear. In view of the coarsening of the class III alloys by slow heating, this phenomenon cannot be explained by assuming a change in quantity or distribution of the dispersed phase. Microscopic examination of the class III alloys after heating and quenching showed that there was no apparent change in microstructure produced by differences in heating rate.

The microstructures of the various samples as-rolled and as-quenched from the two different heating temperatures showed that the microstructures predicted were realized. However, as indicated above, the second phase in the 0.5 per cent Si alloy and the 8 per cent Mg alloy is essentially dissolved at the lower annealing temperature of 750° F.

It is interesting to note that the diffraction patterns of the two alloys, aluminum plus 3 per cent Mn and aluminum plus 0.3 per cent Ti, revealed that, all other factors being the same, the sample that was treated at the most rapid heating rate tended to have the greatest power for recrystallization; that is, recrystallization began at lower degrees of deformation. This greater recrystallization power of the samples heated at the more rapid rate may be caused by the effect of recovery, assuming that recovery does decrease the recrystallization capacity of cold-worked metals. It is suggested that prior to recrystallization some recovery may occur as a function of heating rate, the greater lapse of time to reach the temperature at which recrystallization occurs permitting a greater degree of recovery to take place.

Part 2. Recrystallization of Cold-worked High-purity Aluminum

Most studies of recrystallization consist of the determination of grain sizes after considerable coalescence has occurred. The relationship of the grain size just after complete recrystallization is of considerable practical and theoretical importance. In a previous paper[1] it has been shown that for a given material, the grain size in alpha brass just after complete recrystallization is essentially independent of the annealing temperature or the time at the temperature and is dependent only upon the degree of cold deformation given to the specimen before the last annealing treat-

[1] L. W. Eastwood, A. E. Bousu and C. T. Eddy: *Trans.* A.I.M.E. (1935) **117**, 246.

ment. A similar investigation was carried out on aluminum of high purity, containing about 0.005 per cent Cu, 0.02 Fe, 0.01 Si and 99.95 Al.

Experimental Procedure

The high-purity aluminum was cast into ingots 3½ by 3½ by 12 in., which were then hot-forged to bars approximately ¾ in. square. These bars were cold-rolled with intermediate annealing periods to 0.20 in. This stock was then cut into 4-in. lengths and machined to wedges. The wedges were annealed and cooled slowly in the furnace to precipitate the soluble constituents. They were then cold-rolled, the wedge-shaped specimen producing a deformation gradient varying from 0 per cent at the small end to about 22 per cent at the large end. These specimens were then annealed by rapidly heating to various temperatures for various periods of time.

In a similar fashion, some of the cold-rolled strips 0.2 in. thick were cut into 10-in. lengths and machined to give a bar tapering toward the center. After the machining operation, the tapered tensile bars were also given an anneal at 650° F. and slowly cooled in the furnace. They were then broken in tension, thus producing a deformation gradient in the bars from about 20 per cent reduction in area in the center of the constricted area to 0 per cent at the large end near the grip section. Thus, two sets of deformation gradient bars were prepared, one by cold-rolling and the other by cold-stretching. The grain size before the final rolling or stretching operation was 0.25 mm. The specimens were then given various annealing treatments, using rapid heating rates in every instance. The longer the time and the higher the temperature of the anneal, the more complete is the recrystallization, using this term as defined above. Generally, there would be one part of the bar corresponding to a definite degree of deformation that would be just completely recrystallized. At places having a higher degree of deformation, the bar would be completely recrystallized with possibly some coalescence. At lower degrees of deformation, recrystallization would be either partial or would not have occurred to any degree. It was thus possible to obtain grain sizes just after complete recrystallization without any coalescence. A specimen of this type has the advantage that all degrees of deformation are represented on one specimen, thus reducing to a considerable extent the number of specimens and the quantity of work required to obtain data on the grain sizes after recrystallization without coalescence. It was shown in the previous work on alpha brass (see ref. 1) that the general deformation gradient did not have any effect upon the grain size produced. After the annealing treatment, the specimens were etched and grain counts made on the surface at the point at which recrystallization was just complete and at other points along the bar where recrystallization had occurred.

Discussion of Results

The grain size obtained at the point at which recrystallization was just complete in the rolled bars is shown in Table 6 and by Fig. 1; the data for the stretched bars are shown in Table 7 and by Fig. 2. The figures show that within the limits of experimental error the grain size for a given material and type of deformation is dependent only upon the degree of deformation and is independent of the temperature or the time of heating, provided no coalescence has occurred after recrystallization is complete.

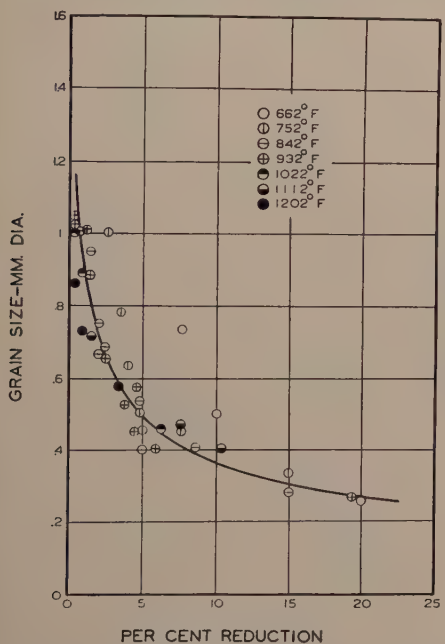

FIG. 1.

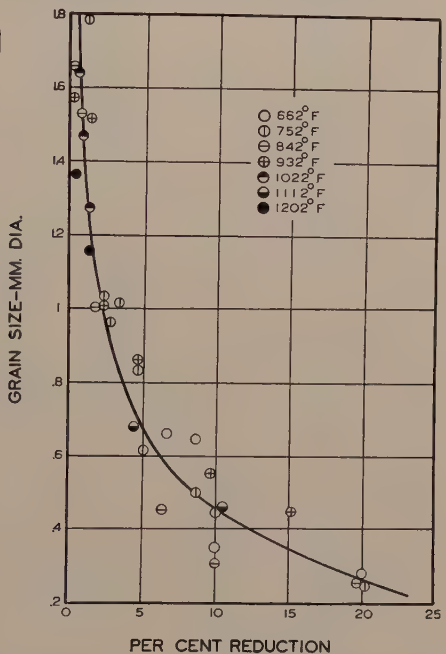

FIG. 2.

FIG. 1.—RELATIONSHIP OF DEGREE OF DEFORMATION BY ROLLING TO GRAIN SIZE OF ANNEALED 99.95 PER CENT ALUMINUM AFTER RECRYSTALLIZATION IS COMPLETE.

FIG. 2.—RELATIONSHIP OF DEGREE OF DEFORMATION BY STRETCHING TO GRAIN SIZE OF ANNEALED 99.95 PER CENT ALUMINUM AFTER RECRYSTALLIZATION IS COMPLETE.

There is, of course, some variation in the data, as might be expected, since it is difficult to get uniform reduction, particularly at low degrees of deformation. It is also true that in a high-purity metal such as this the grain sizes are relatively coarse, and, as a consequence of the smaller number of grains present, the possibility of a variation in the average grain size is great.

A similar experimental procedure carried out on aluminum of decidedly lower purity shows in general a similar relationship. As compared with the high-purity aluminum, it appears that the grain size of the low-purity aluminum at moderate or high degrees of cold deformation is finer than

TABLE 6.—*Heat-treatment and Grain Size, Rolled Specimens of High-purity Aluminum*

Heat-treatment		Recrystallization Complete	
Annealing Temperature, Deg. F.	Time at Anneal	Minimum Reduction, Per Cent	Grain Size, Mm. Dia.
662	180 min.	20.0	0.25
662	300 min.	10.0	0.51
662	480 min.	7.5	0.74
752	15 min.	15.0	0.33
752	30 min.	7.5	0.43
752	60 min.	5.0	0.46
752	120 min.	4.7	0.51
752	180 min.	3.7	0.64
752	300 min.	3.0	0.79
752	480 min.	2.5	1.04
842	30 sec.	15.0	0.28
842	1 min.	8.5	0.41
842	5 min.	5.0	0.41
842	15 min.	4.7	0.53
842	30 min.	4.5	0.58
842	60 min.	2.2	0.69
842	120 min.	2.0	0.76
842	180 min.	1.5	0.94
842	300 min.	1.0	1.04
932	5 sec.	20.0	0.25
932	15 sec.	6.0	0.41
932	30 sec.	4.5	0.43
932	1 min.	3.5	0.53
932	5 min.	2.5	0.66
932	15 min.	1.7	0.89
932	30 min.	1.0	1.04
932	60 min.	0.8	1.17
932	120 min.	0.5	1.27
1022	30 sec.	6.5	0.46
1022	1 min.	2.2	0.69
1022	5 min.	1.0	0.89
1112	2.5 sec.	10.5	0.41
1112	5 sec.	7.5	0.46
1112	15 sec.	1.5	0.71
1112	1 min.	0.5	1.02
1202	2.5 sec.	3.2	0.58
1202	5 sec.	1.2	0.71
1202	15 sec.	0.5	0.86

TABLE 7.—*Heat-treatment and Grain Size, Stretched Specimens of High-purity Aluminum*

Heat-treatment		Recrystallization Complete	
Annealing Temperature, Deg. F.	Time at Anneal	Minimum Reduction, Per Cent	Grain Size, Mm. Dia.
662	120 min.	20.0	0.28
662	180 min.	10.0	0.36
662	300 min.	8.0	0.64
662	480 min.	6.5	0.69
752	5 min.	20.0	0.25
752	15 min.	10.0	0.46
752	30 min.	8.3	0.51
752	60 min.	5.0	0.61
752	120 min.	4.5	0.84
752	180 min.	3.0	1.14
752	300 min.	2.5	1.17
752	480 min.	2.0	1.83
842	30 sec.	20.0	0.25
842	1 min.	10.0	0.31
842	5 min.	6.7	0.46
842	15 min.	2.0	1.02
842	30 min.	1.0	1.52
842	60 min.	0.5	1.65
932	5 sec.	15.2	0.46
932	15 sec.	9.5	0.56
932	30 sec.	4.5	0.86
932	1 min.	3.0	1.02
932	5 min.	1.5	1.52
932	15 min.	0.5	1.57
932	30 min.	0.5	1.57
1022	30 sec.	1.5	1.27
1022	1 min.	1.0	1.47
1022	5 min.	0.5	1.65
1112	2.5 sec.	10.2	0.46
1112	5.0 sec.	4.3	0.69
1112	15.0 sec.	2.5	0.97
1202	2.5 sec.	1.5	1.17
1202	5.0 sec.	0.5	1.37

that obtained with the pure aluminum. The reverse is true, however, at low degrees of deformation; that is, coarser grains, generally columnar grains, are formed in the aluminum of low purity after recrystallization of the slightly deformed material. This growth of columnar grains may be a function of preferred orientation and mechanical fibering in the specimen.

Summary

Three different classes of aluminum-base alloys have been investigated. The first class consists of a single phase at all temperatures between the solidus and room temperature, the second class consists of a single phase at temperatures near the solidus and two phases at room temperature, while the third class of alloys consists of two phases at all temperatures below the solidus line. It has been found that the grain size after annealing or heat-treating the cold-worked materials of the first class is unaffected by heating rate. The second class of material, which contains a second phase completely soluble at high temperatures, is unaffected by heating rate within the limits of these experiments provided the soluble materials have been completely dissolved during the heating operation, thus leaving a single-phase material. If the temperature is such that the soluble materials remain in part undissolved, this class of alloys is affected by heating rate much as in class III. It has been found that alloys of class III—i.e., materials that contain a second essentially insoluble phase dispersed in the aluminum-rich matrix—produce a coarser grain when the cold-worked material is slowly heated than when rapidly heated.

An investigation of the grain size of high-purity aluminum shows that if recrystallization of the cold-worked material is just complete—that is, if no coalescence has occurred—the grain size is independent of the time and the temperature of the anneal and, for a given material, is dependent only upon the degree of deformation. In this respect, high-purity aluminum is similar to alpha brass.

DISCUSSION

(*W. P. Sykes presiding*)

P. A. Beck,* Barber, N. J. (written discussion).—This paper contains the best data now available on the effect of the heating rate on the recrystallized grain size. Another point that is well demonstrated by the authors' work is that the heating rate effect is *not* found whenever the grain size is determined by grain growth† (coalescence)

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* Central Research Laboratory, American Smelting and Refining Co.

† In this discussion I will adhere to the nomenclature used by Dr. R. F. Mehl in his article on Recrystallization, Metals Handbook 1939. The authors of the present article use the term "coalescence" in the sense that "grain growth" is used by Dr. Mehl.

or by a combination of recrystallization and grain growth rather than by recrystallization alone. Such conditions have been shown to exist at the higher annealing temperature (950° F.) for both class I and class II alloys. The question arises whether or not the apparent absence of the effect with class I (single-phase) alloys at the lower annealing temperature (750° F.) is also due to the same cause; namely, grain growth. That grain growth actually occurs at that temperature, at least if the deformation is high, has been pointed out by the authors themselves. However, the question still remains open for the lower deformations. It is, of course, difficult to decide whether or not grain growth has occurred. Furthermore, the authors state that in this region, where the number of grains per square millimeter is small, their grain counts are less accurate. Consequently, it might perhaps be even questioned whether the heating-rate effect is actually absent. Such doubts are substantiated by the data on 2 per cent Zn alloy in Table 2. The only samples of this alloy that have attained fully recrystallized structure, yet probably did not undergo grain growth, are those with 10 per cent deformation, and for this deformation the table actually shows a heating-rate effect in the right direction. But even if there be no effect, in the range of heating rate here used, the effect might well be obtained, for instance, if the heating rates were lower. Therefore, as long as these questions remain open, we are facing at least three possible conclusions regarding the heating-rate effect in the absence of grain growth:

The first conclusion, that of the authors, is that the heating-rate effect is absent whenever the alloy consists of a single phase and is present if the alloy has more than one phase.

The second possibility is that the heating-rate effect always occurs whenever grain growth is definitely excluded. From the standpoint of the second possibility, it is of no importance whether the alloy consists of one or of two phases. The decisive factor is the occurrence or absence of grain growth. The presence of a second phase is important only in so far as it retards or suppresses grain growth, and thus extends the range in which the grain size is determined by recrystallization alone.

Which of the two conclusions, if either, is correct cannot be decided on the basis of the data here presented. However, I would like to refer to the well-known painful experience of several investigators in their efforts to produce single crystals of pure metals and of solid solutions by the recrystallization method; namely, that the samples have to pass extremely slowly through the critical temperature range where recrystallization is just beginning. If the heating rate is too high, so that the first new crystal has no time to absorb all of the deformed material before a certain somewhat higher temperature is reached, some additional new grains will start to grow and the sample becomes a polycrystal instead of a single crystal. This would indicate that the heating-rate effect may exist even if there is no second phase present.

The third possibility, and perhaps the most likely one, is that, while the presence of a second phase enhances the effect of the rate of heating, this effect may also occur in single-phase metals, at least under certain conditions, such as low deformations and low rates of heating.

In the second part of their paper the authors show that in the deformation and temperature range used in their work, the effect of the annealing temperature on the grain size is relatively small. That there is some effect is, however, clearly shown by their own Fig. 1. Of the three points, corresponding to the annealing temperature of 662° F., two are very considerably high, the third one is on the curve. Of the seven points, corresponding to the annealing temperature of 752° F., five are too high, one is on the curve, and one is below. These large grain sizes, corresponding to the two lowest annealing temperatures, seem to have been ascribed by the authors to the scattering of the data. I feel, however, that we are justified in trusting their data more than they do themselves, and in interpreting these systematic deviations in accordance with previous experience. Should the authors extend their observations

to still lower annealing temperatures, and give their samples long enough anneals to cause recrystallization at small deformations, they would probably find still larger grain sizes, in accordance with the single-crystal experience referred to above. There cannot be much doubt that in this region the grain size actually increases with decreasing temperature.

The fundamental solution of all these problems could be most adequately given in terms of the two factors of recrystallization: number of nuclei and velocity of growth. The effect of varying temperature, of deformation and of minor additions on both of these factors should be studied separately. The near independence of the recrystallized grain size from the annealing temperature, as found by the authors within certain limits, means either that both factors are independent of temperature, or, more likely, that both the number of nuclei and the velocity of growth increases with increasing temperature in such a way as to nearly balance each other's influence on the grain size. It seems, however, that with decreasing temperature this balance is gradually offset by the fact that the number of nuclei is decreasing more rapidly than the velocity of growth, resulting in fewer and larger grains. The major effect of a second phase is to decrease the linear velocity of growth both in grain growth (coalescence), and in recrystallization. This is nicely confirmed by the present authors' work.

Z. Jeffries,* Cleveland, Ohio (written discussion).—The authors are to be congratulated for the presentation of many new facts on grain growth. They have set forth the factual data clearly so that they are available to all metallurgists in the future. Workers in this field realize that it is difficult to exactly reproduce grain size in duplicate experiments: furthermore, it is difficult to measure it exactly. Within such limits, however, it may be expected that other investigators would presumably duplicate the results reported by these authors.

Although the results reported could not be specifically predicted, apparently they are not inconsistent with many investigations that have been reported in the past. Furthermore, if the alloys containing two phases are considered from the standpoint of one phase acting as a foreign substance to obstruct grain growth, the results fall nicely into existing generalizations. Most of the results may be classified as normal, but there are some abnormalities. For instance, in Table 5 the 99.3 per cent Al sample that was reduced 10 per cent and heated to 950° F. exhibits what may be called abnormal grain growth; that is, the conditions were germinative. The slow heating produced grains ⅛ in. in diameter, whereas the fast heating yielded four grains per square millimeter. On a three-dimension basis, this means that the rapidly heated piece had about two hundred times as many grains as the piece that was heated slowly. While this is not an extreme case of germination, it is definite.

Presumably, this result was produced by even heating; that is, with no substantial temperature gradients. When strong temperature gradients are introduced, greater abnormality may obtain. Under such conditions, even single-phase metals may show abnormal grain growth. Grain growth in tungsten, under certain conditions, is one good example, and the production of single crystals of silicon steels by Ruder is another. Presumably, both the tungsten and the silicon steels may be regarded for practical purposes as single-phase metals. Ruder's experiments with silicon steels consisted of mildly deforming strips at room temperature, then heating one end to a temperature in the grain-growth range and passing the strip through the highly heated zone at a rate not faster than the velocity of grain growth. In this way, a large crystal formed originally at one end of the strip may grow at the expense of all the other grains or grain fragments, thus producing a single crystal.

* General Electric Co.

Another method of producing single crystals in some metals is to moderately strain the whole specimen and then heat slowly to a very high temperature. Heating rapidly to the very high temperature may result in many grains: in such cases the heating rate is important even though there are no substantial temperature gradients.

It is interesting that the authors' results point to the presence of a second phase in the grain-growth temperature range as a factor affecting abnormal growth. It is probable that there are nonmetallic impurities present, which also have a bearing on grain growth, and that these may modify the results somewhat.

The authors interpret their X-ray data as suggesting that the samples heated at the most rapid rate have a greater capacity for recrystallization than have those heated at slower rates. They state that the salt bath used for rapid heating was superheated slightly to compensate for the temperature loss when the samples were immersed. May it not be possible that the samples so immersed actually received a different heat-treatment from those treated in muffles? In other words, may not the samples heated in the salt bath have actually been given a higher temperature treatment than those treated in the muffle?

L. W. Kempf,* Cleveland, Ohio (written discussion).—The authors have made a distinct contribution to our knowledge of recrystallization phenomena. The structural characteristics of metals have long been known to have a considerable effect on its recrystallization characteristics. In this paper the authors have begun the quantitative definition of these effects. The internal structure has been demonstrated to have marked effect on recrystallization characteristics, perhaps also some attention should be directed to the effect of external or gross shape on recrystallization and grain growth. Most of the phenomena referred to by Dr. Jeffries as abnormal grain growth have been observed in fine wire or thin sheet where at least one surface of the grain lies in the bounding surface of the structure itself. It appears conceivable that the recrystallization and grain-growth tendencies of the metal would be different when completely surrounded by other similar grains than when a portion of the grain was an external surface of the structure. Perhaps even mechanical fibering in a polyphase material might function in a manner similar to an external surface.

D. W. Smith,† New Kensington, Pa. (written discussion).—Dr. Jeffries and Dr. Beck have pointed out that in order to produce single crystals by the "strain-anneal" method it is necessary to gradually raise the temperature after straining. They emphasized that if the temperature is raised too rapidly, a polycrystalline structure results. I should like to point out that if the raising of the temperature is too gradual at low temperatures, a polycrystalline structure also results.

The following procedure is used at the Aluminum Research Laboratories for making single-crystal bars of high-purity aluminum:

1. The desired shape and size of bar is machined from hard-rolled slab.
2. The bar is then annealed 6 hr. at 550° C.
3. The annealed bar is then stressed in tension to produce a permanent elongation of 1.5 to 2.0 per cent in the gauge length.
4. The strained bar is put in a furnace at 450° C.; i.e., the bar is heated rapidly to this temperature, and held for 24 hours.
5. The temperature of the furnace is raised 20° C. per day until 600° C. is attained.
6. Finally, the bars are annealed 48 hr. at 625° to 650° C. and furnace-cooled to room temperature.

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* Aluminum Research Laboratories, Aluminum Company of America.

† Aluminum Research Laboratories.

If the strained bars are put in a cold furnace and heated more slowly to 450° C., no recrystallization or grain growth occurs during the treatment, and the grain structure remains substantially as it was after the first anneal of 6 hr. at 550° C.

F. T. McGuire,* Cambridge, Mass. (written discussion).—One point must be proved before we can accept the conclusion that in aluminum alloys consisting of two phases the heating rate affects the grain size in such a way that the large grain size is obtained by slow heating; that is, that recrystallization has not been completed earlier in the slower heating with coalescence causing the grain size to become larger. This point could be proved by annealing at a somewhat lower temperature, which would require a longer time, and in this way make the difference in time of heating to temperature for the slowly heated specimen and the rapidly heated specimen rather insignificant compared to the time at temperature. A further check would be to keep some of the rapidly heated specimens at temperature for various lengths of time in order to show that the coalescence obtained is not sufficient to account for the larger grain size of the slowly heated specimen.

The authors conclude that the recrystallized grain size of single-phase alloys is not a function of heating rate. It seems to me that there should be the same dependence of grain size on heating velocity as in the two-phase alloys. I believe that the results obtained in the 99.95 per cent Al alloy given a 5 per cent reduction that show the same grain size for all heating rates may be explained on the basis of coalescence erasing a possible difference in grain size. This could be cleared up by making time at temperature a variable to conclusively prove the point.

The authors have mentioned that the grain sizes listed may actually be the result of recrystallization plus some coalescence. These two phenomena are not distinct and this point demands great emphasis. It is highly improbable that there is not an overlap of the two. Thus the grain size listed in any case could never be larger than that observed but may be much smaller, and the difference being accounted for by coalescence before recrystallization in the specific sense is completed.

L. W. Eastwood and R. W. James (written discussion).—Dr. Beck has raised some interesting points. Of the three possible conclusions he has made, the first coincides with that made by the authors. The second has an element of possibility in it, but class I alloys annealed at 750° F. after *low deformation* undergo very little or no coalescence after recrystallization. However, the data indicate that no heating-rate effect exists, hence Dr. Beck's second conclusion appears somewhat doubtful. Since the data are not complete, Dr. Beck has raised a point worthy of further study. Certainly, as pointed out on page 130, subsequent coalescence may eliminate previously existing heating-rate effects.

The temperatures and heating rates used in this investigation are limited to a range corresponding roughly to that which might be encountered in commercial procedures. Of course there is an enormous range of heating rates slower than those used by the authors. The conclusions in this paper necessarily can apply only to the range of variables covered in this investigation. The well-known observations regarding the production of single crystals cited by Dr. Beck are very interesting, but the conditions involved in these procedures are considerably outside of the range of heating rates used in this investigation. They are also outside the heating-rate limits generally encountered in commercial operations.

Dr. Beck has attached some significance to certain scattering of the data on grain sizes obtained after annealing at 662° F. It will be observed in Figs. 1 and 2 that only two of the seven points lie higher than the normal scattering of the rest of the data.

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* Graduate School of Metallurgy, Harvard University.

If there were a real coarsening at low temperatures, as suggested by Dr. Beck, it should be more consistently apparent. However, since the data are obviously inadequate in the low-temperature, long-time anneal range, the point is worth checking further.

Dr. Jeffries's reference to the 99.3 per cent Al sample reduced 10 per cent and heated slowly to 950° F. (Table 5) is interesting. According to the generally accepted view expressed by Dr. Jeffries in "The Science of Metals," "normal" grain growth occurs when the grain size is larger the higher the heating temperature, the longer the time at temperature and the lower the degree of deformation, *all other factors being the same.* "Abnormal" grain growth, therefore, must occur when the above generalizations do not hold. Table 5 shows that the particular specimen referred to follows the normal grain-growth "laws," at least on the basis of the limited data in the table. It is true that this sample had an unusually large grain size, but should this be considered a real instance of "abnormal" growth? Perhaps a revised definition of "abnormal" grain growth is desirable to reconcile the divergent opinions that seem to exist. All of the data presented in this paper are in accord with the general principles of "normal" grain growth cited above.

There are no doubt some relatively rare cases of real "abnormal" grain growth; that is, growth that does not conform to the present accepted "laws" of recrystallization. An explanation for such growth along the lines suggested by Mr. Kempf appears logical, though it must be admitted that no systematic investigation has been made. A study of these effects would perhaps serve to clarify the present status of the so-called "abnormalities" that are sometimes encountered in investigations involving recrystallization.

Dr. Jeffries suggests that the greater capacity for recrystallization noted in the rapidly heated specimens may actually be a function of the different heat-treatment involved by slightly superheating the bath to correct for the temperature drop when the specimens were immersed. While this raises a point apparently worthy of some consideration, additional information concerning the experimental procedure, which was not included in the paper, may explain why the authors do not feel that the samples in question were significantly overheated. The specimens were loosely packed in large bundles with dividers providing considerable space between the aluminum strips. When the bundles were immersed in the bath they were moved about to assure immediate and complete contact of the specimens and the fused salt. The pyrometer indicated that the bath dropped to the desired temperature in less than one minute. Making some allowance for pyrometer lag and for the time required for the center of the strips to come up to temperature, it seems rather improbable that there could have been any appreciable overheating. It is possible that the surface of the strips may have momentarily exceeded slightly the intended temperature but this seems of little consequence inasmuch as all microscopic and X-ray data were obtained from distinctly subsurface planes.

Mr. McGuire suggests that the heating-rate effect may really be nonexistent, the effect noted being a result of holding the specimen a longer time at elevated temperature. He suggests that when the specimens are slowly heated the grains are coarser because of coalescence. This explanation is attractive because it is so simple. However, it is well known that a second phase, which acts as an obstruction to grain growth, retards coalescence. Hence, if this explanation were correct, a heating-rate effect should not be pronounced in a two-phase alloy such as those listed in Table 4, but should be quite evident in the single-phase alloys of Table 2. Obviously the opposite is true.

The point raised by Mr. McGuire in his third paragraph has been covered in the reply to Dr. Beck's discussion.

Development of Abnormally Large Grain Sizes in Rolled and Annealed Copper Sheet

By Maurice Cook* and C. Macquarie†

(Detroit Meeting, October, 1938)

Normally the grain size of cold-rolled and annealed copper sheet is of the order of 0.02 to 0.06 mm., and 0.1 mm., for example, would, for many purposes, be regarded as undesirably large. The occurrence of very large grain sizes in a few isolated cases of copper sheet led the authors to inquire into the causes giving rise to such unusual results. During the course of this work a very large number of experiments have been carried out to determine the effect of varying the conditions of the final and penultimate rolling and annealing operations, as well as of earlier rolling and annealing treatments. A correspondingly large number of observations have been made, but within the space of one paper it is possible only to outline relatively briefly what appear to be the more important of these experiments and observations. The presentation of the results does not follow chronologically the order in which the experiments were carried out and they have been rearranged for the sake of simplicity.

In recent years a considerable amount of work has been done in connection with the recrystallization and grain growth in metals and alloys that take place on annealing, and a number of generalizations have been reached. It is known that the crystal size in wrought material in the annealed condition depends on a number of factors, including the time and temperature of the annealing operations and the nature and amount of cold-work to which the material has been subjected. Results, however, that are not covered by these generalizations can be obtained, which, in some instances, may even appear to be contradictory to them. According to these generalizations gradual changes in grain size are effected by progressive variation of the factors involved in annealing or cold-working. The work recorded in the present paper, however, relates to the development of grain sizes which are far beyond those normally encountered in ordinary annealing operations and far in excess of grain sizes which,

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* Deputy Research Manager, I.C.I. Metals Limited, Kynoch Works, Witton, Birmingham, England.

† Research Metallurgist, I.C.I. Metals Limited, Kynoch Works.

according to ordinary standards, would be classified as coarse or large. Moreover, the development of these is often brought about quite abruptly during the progressive alteration of some one factor in the annealing or rolling operations.

Experimental Procedure

When abnormally large crystal sizes such as those discussed in this paper are being considered, the use of numerical values in millimeters is not very satisfactory, because the variation in size is frequently considerable. The presentation of results in graphical form is scarcely more satisfactory because of the enormous difference between strip possessing grain sizes of the usual order and that showing an abnormally large grain size. The grain-size results are given in the form of tables and the letter *L* is used to denote what is regarded as an abnormally large crystal size, which means that the strip contains, and, in fact, is composed for the main part of, crystals that, generally speaking, are at least 20 or 30 mm. across and range in size up to 60 or 80 mm. and even more.

As will be seen later, large crystals are obtained only in certain qualities of relatively pure copper by observing the conditions that have been established, and with less pure copper and copper lightly alloyed deliberately, large crystals are not produced when the same rolling and annealing procedure is followed. While the paper is concerned only with the effect of rolling and annealing conditions on the development of abnormally large grain sizes, a few experiments on annealing standard tensile-test pieces of copper strip were made and may be noted briefly, although they yielded negative results.

Standard tensile-test pieces 2 in. long and ½ in. wide in the gauge portion were cut from soft O. R. C. copper strip 0.064 in. thick, normal to the rolling direction. (For composition, see Table 11.) Test pieces were stressed in a tensile machine and two series obtained with permanent extensions of 1, 2, 3, 4, 5, 10, 20, 30, 40, and 50 per cent. Specimens from the series of test pieces cut normal to the rolling direction were annealed at 450°, 550°, 650°, 750° and 850° C. for one hour, but no abnormally large grain size was developed, the limits of 0.02 or 0.03 to 0.06 mm. covering the whole combination of extensions and annealing temperatures. In view of these results, specimens from the series of test pieces cut in the rolling direction and subjected to different extensions were annealed only at 550° and 850° C. for one hour and the resulting extreme limits of grain size were 0.03 to 0.05 or 0.06 mm. It is of interest to note that this material from which the tensile-test pieces were cut developed a large crystal size (of the order of 20 mm.) when it was reduced 50 per cent in thickness by cold-rolling in a direction normal to the previous rolling and finally annealed for one hour at 800° C.

Development of Large Crystals in Straight-rolled Metal

The basis material for most of the experiments was copper strip about 0.45 or 0.50 in. thick, which originally was hot-rolled from O.R.C. ingots measuring approximately 40 in. in length, 24 in. in width and 3½ in. in thickness, and weighing about 1000 lb. Numerous preliminary experiments showed that essential conditions for developing abnormally large crystal sizes in the particular quality of copper under consideration were a high final annealing temperature and a heavy final cold-rolling reduction.

Effect of Final Annealing Temperature.—In order to determine the effect of the final annealing temperature, strip hot-broken down to 0.45-in. thickness from the original ingot thickness of 3½ in. was cold-rolled without any intermediate annealing to a thickness of 0.008 in., corresponding to a reduction of 98 per cent. Samples of this material were annealed for one hour at temperatures ranging up to 1000° C. Grain-size measurements were made after the annealing treatments, and the results are given in Table 1, which shows that the increase in grain

Table 1.—*Effect of Final Annealing Temperature*

Material Hot-rolled to 0.45 In., Cold-rolled to 0.008 In. (98 Per Cent Reduction), Annealed One Hour.

Annealing temperature, deg. C.	500	600	700	800	850	900	925	950	975	1000
Grain size, mm.	0.03	0.03–0.04	0.04	0.04	0.04–0.05	0.04–0.05	0.04–0.05	0.05	0.07–0.10	*L*

size in raising the final annealing temperature from 500° to 975° C. is relatively slight. When, however, the annealing temperature is raised to 1000° C. a remarkably large crystal structure results (Fig. 1). Fig. 2 shows the structure of the same copper subjected to identical rolling and annealing treatments, except that the final annealing was carried out at 900° instead of at 1000° C.

Table 2.—*Effect of Cold-rolling Reduction*

Material Hot-rolled to 0.45 In., Cold-rolled and Finally Annealed One Hour at 1000° C.

Cold-rolling reduction, per cent.	4.2	11.4	25.0	53.2	75.4	89.8	92.0	95.0	96.0	96.8	98.0
Grain size, mm.	0.04	0.04	0.04–0.05	0.04–0.05	0.05	0.08	0.1	*L*	*L*	*L*	*L*

Effect of Cold-rolling Reduction.—To determine the effect of the magnitude of the cold-rolling reduction following hot-rolling, strip hot-broken down to 0.45 in. thick from the original 3½-in. ingot was cold-

rolled without any annealing down to 0.008 in., corresponding to a cold reduction of 98 per cent, and samples were taken at various stages of cold-rolling. These were then all annealed for one hour at 1000° C. The

Fig. 1.—Large crystal structure developed by annealing at 1000° C. Natural size.

resulting grain sizes are indicated in Table 2, which show that, providing the cold-rolling of the hot-broken strip exceeds about 96 per cent, very large crystal sizes similar to that shown in Fig. 1 are developed on

annealing at 1000° C. Fig. 3 illustrates the very much finer structure obtained in the same material, finally annealed at 1000° C. when the cold-rolling reduction is 92 per cent.

To obtain still more information relative to the amount of cold-rolling, prior to finally annealing at 1000° C., a hot-rolled strip 0.45 in. thick was cold-rolled to the different thicknesses shown in Table 3.

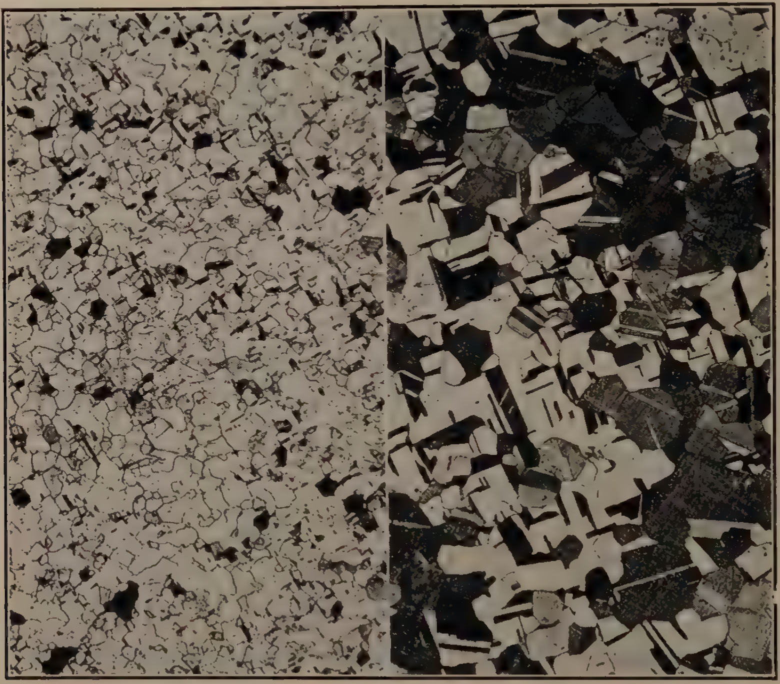

FIG. 2. FIG. 3.

FIG. 2.—SAME COPPER AS IN FIG. 1 BUT ANNEALED AT 900° C. × 50.
FIG. 3.—FINE STRUCTURE IN MATERIAL ANNEALED AT 1000° C. WHEN COLD-ROLLING REDUCTION IS 92 PER CENT. × 50.

These materials were all annealed at 600° C. for one hour and then cold-rolled to the same final thickness; that is, 0.008 in. The grain sizes of these specimens, subjected to a final cold-rolling reduction of the magnitude indicated in Table 3, are included in the same table. The results not only confirm those obtained from the experiments recorded in the previous paragraph, but show that the large cold-rolling reduction and high final annealing temperature necessary for the production of large crystals obtain, irrespective of whether the material was in the hot-rolled state or in the fully annealed condition after a relatively light or very severe cold-rolling, following the initial hot-rolling.

Effect of Total Amount of Cold-rolling and Temperature of Penultimate Annealing.—The foregoing experiments indicate clearly the necessity

TABLE 3.—*Effect of Final Cold-rolling Reduction*

Material Hot-rolled to 0.45 In., Cold-rolled to Thicknesses Indicated, Annealed at 600° C. One Hour, Cold-rolled to 0.008 In., and Annealed One Hour at 1000° C.

Initial gauge, in.	0.400	0.350	0.300	0.250	0.200	0.150	0.140	0.125	0.100	0.075	0.060	0.050	0.040	0.030	0.020	0.015	0.012	0.009
Final cold-rolling reduction, per cent	97.9	97.6	97.3	96.7	96.0	94.6	94.4	93.4	92.0	89.4	86.5	84.9	80.0	73.3	60.0	46.5	33.3	12.5
Grain size, mm.	*L*	*L*	*L*	*L*	10/20	2/3	0.1	0.07–0.08	0.1–0.2	0.06–0.07	0.05–0.06	0.08	0.1–0.2	0.1	0.1	0.08	0.04	0.05–0.06

TABLE 4.—*Effect of Penultimate Annealing Temperature*

Material Hot-rolled to 0.45 In., Cold-rolled to 0.08 In. (82 Per Cent Reduction), Annealed One Hour at Temperatures Given, Cold-rolled to 0.008 In. (90 Per Cent Reduction) and Finally Annealed One Hour at 1000° C.

Penultimate annealing temperature, deg. C.	1000	900	800	700	675	650	625	600	575	550	525	500	400	300	200	150	Unannealed
Grain size, mm.	0.1–0.2	0.07–0.08	0.04–0.05	0.04–0.05	0.03–0.04	0.03–0.04	0.03–0.04	0.04–0.05 & 2/3	10–15	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*

for a high final annealing temperature and a heavy final cold-rolling reduction. Some further observations were made to determine the effect of interposing an intermediate annealing in the cold-rolling carried out to effect the reduction from the hot-rolled material at a thickness of 0.45 in. down to a final thickness of 0.008 in. In this series the hot-rolled strip was reduced to 0.08 in. by cold-rolling, corresponding to a reduction of 82 per cent. Samples cut from it at this stage were then annealed at different temperatures ranging up to 1000° C. as shown in Table 4, and all the samples were then finally cold-rolled to 0.008-in. thickness, which corresponds to a final cold-rolling reduction of 90 per cent. After annealing at 1000° C. the grain sizes in these strips were determined (Table 4) and show that provided the penultimate annealing temperature does not exceed 550° C. very large crystal sizes are obtained with a final rolling reduction of 90 per cent. If the penultimate annealing temperature exceeds 600° C., the grain sizes in the finally annealed materials are normal.

The object of the next series of experiments was to ascertain, with metal hot-rolled to 0.45 in. thick, the smallest final cold-rolling reduction that would bring about large grain sizes when finally annealed at 1000° C. with an intermediate annealing at 550° C. introduced. For this purpose hot-rolled strip at 0.45 in. was cold-rolled to the various gauges indicated in the second column of Table 5. All the materials were then annealed

TABLE 5.—*Effect of Interposing an Annealing Operation of One Hour's Duration at* 550°C. *at Different Stages in a Total Cold-rolling Reduction of* 98.2 *Per Cent*

Material Finally Annealed One Hour at 1000° C.

Initial Gauge, In.	Gauge for Intermediate Annealing, In.	Final Gauge, In.	First Reduction, Per Cent	Percentage of Total Reduction	Second Reduction, Per Cent	Percentage of Total Reduction	Grain Size, Mm.
0.450	0.400	0.008	11.0	11.3	98.0	88.7	*L*
0.450	0.350	0.008	22.3	22.6	97.5	77.4	*L*
0.450	0.300	0.008	33.3	34.0	97.0	66.0	*L*
0.450	0.250	0.008	44.2	45.2	96.5	54.8	*L*
0.450	0.200	0.008	55.5	56.7	96.0	43.3	*L*
0.450	0.150	0.008	66.6	68.0	94.5	32.0	*L*
0.450	0.100	0.008	77.5	79.1	92.0	20.9	*L*
0.450	0.075	0.008	83.0	84.5	89.0	15.5	*L*
0.450	0.060	0.008	86.8	88.0	86.5	12.0	*L*
0.450	0.050	0.008	89.0	90.5	84.0	9.5	15–20
0.450	0.040	0.008	91.0	93.0	79.5	7.0	10–15
0.450	0.030	0.008	93.1	95.4	73.2	4.6	10–15
0.450	0.020	0.008	95.5	97.5	60.0	2.5	10–15
0.450	0.015	0.008	96.5	98.5	46.5	1.5	15–20
0.450	0.010	0.008	97.8	99.5	20.0	0.5	0.05–0.06

at 550° C. and finally cold-rolled to 0.008-in. thickness. The amount of the first cold-rolling reduction is given in the fourth column of Table 5 and the amount of the second, or final, cold-rolling reduction in the sixth column. The values given show that a large crystal size is obtained by finally annealing at 1000° C. with a final cold-rolling of 85 per cent or more, provided the penultimate annealing temperature is of the order of 550° C.

Development of Large Crystals by Cross Rolling

In the production of sheets it is quite a usual practice to subject the metal at some stage of manufacture to cross rolling and it was, in fact, during the annealing of cross-rolled copper that the presence of very large crystals was first noticed, although these were not as large as those referred to in the foregoing section, and, moreover, there was a considerable difference in the appearance of the two types of large crystals. Preliminary observations showed that if ingots were hot-broken down to about 0.50 in., cold-rolled in the same direction to about 0.064 in., annealed and then cross-rolled, the development of large crystal size depended on the magnitude of the penultimate rolling reduction and of the final cross-rolling reduction and on the temperature of the penultimate and final annealing operations.

Effect of Final Annealing Temperature.—For determining the effect of the final annealing temperature on the grain size, copper produced in the following manner was used: hot-rolled to 0.5 in. from the original ingot thickness of 3½ in., reduced 87 per cent in thickness by cold-rolling to 0.064 in., annealed at 450° C. for 2½ hr. and cross-rolled to 0.026 in. This hard strip was annealed at temperatures varying from 450° to 1000° C. The resulting grain sizes are given in Table 6, and show

Table 6.—*Effect of Final Annealing Temperature*

Material Hot-rolled to 0.5 In., Cold-rolled to 0.064 In. (87 Per Cent Reduction), Annealed at 450° C. Cross-rolled to 0.026 In. (59 Per Cent Reduction) and Annealed One Hour.

Final annealing temperature, deg. C.	400	500	600	700	750	775	800	825	850	875	900	925	950	975	1000
Grain size, mm.	0.03	0.03	0.03–0.04	0.02–0.03	10–15	10–15	10–15	10–12	7–10	7–10	7–8	5–7	2–3	1.0	0.5–1.0

clearly that sheets rolled in accordance with the above procedure develop abnormally large grain sizes if the annealing temperature reaches 750° C. With annealing temperatures above 800° to 850° C., the crystal size gradually decreases until with a final annealing temperature of 1000° C. the grain size, although large according to ordinary standards, is relatively small compared with the maximum obtained by finally annealing at 800° C.

The large crystals produced in this way—that is, on material finally cross-rolled—are of the order of 10 to 30 mm., and, unlike the larger grains produced by straight rolling, they are free from acicular markings and tend to be more equiaxed. A typical specimen is illustrated in Fig. 4. The other outstanding difference between the straight-rolled and the cross-rolled material is that in the former, provided the other necessary conditions are complied with, the grain size increases with the final annealing temperature up to 1000° C., which was the highest used,

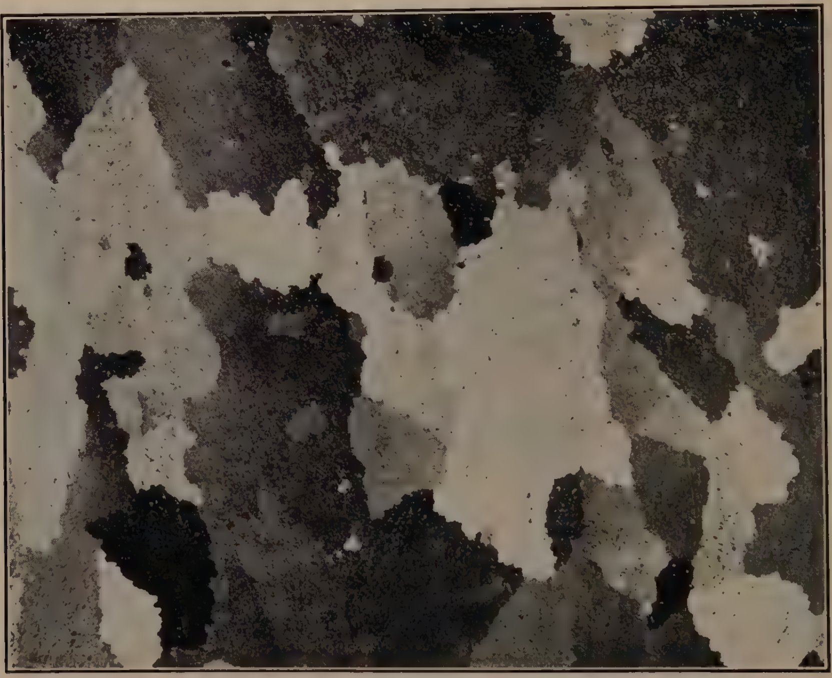

FIG. 4.—LARGE CRYSTALS IN CROSS-ROLLED MATERIAL. NATURAL SIZE.

whereas with the cross-rolled material the grain size reaches a maximum with a final annealing temperature of about 800° C.

Earlier observations, recorded in Table 1, have shown that a temperature of 800° C. for the final annealing operation is not high enough to give rise to large crystals, even with a final cold-rolling reduction of 98 per cent, and if the final annealing were carried out at 1000° C. large grains would not be produced in copper reduced in one stage from 0.5 to 0.026 in., since the reduction is only 94 per cent. (See Tables 2 and 3.)

Effect of the Magnitude of the Final Cross-rolling Reduction.—To determine the effect of the magnitude of the final cross-rolling reduction, strip produced at a thickness of 0.064 in. by the process outlined above was annealed at 450° C. and cross-rolled to gauges ranging from 0.058 to 0.010 in., corresponding to reductions of 10 to 90 per cent in thickness.

Some of the same material at a thickness of 0.064 in. was, after annealing at 450° C., rolled in the same direction as the previous rolling, to the same range of gauges. All the samples were then finally annealed for one hour at 800° C. The grain sizes on the resulting strips are detailed in Table 7,

TABLE 7.—*Effect of Varying Amounts of Cold-rolling*

Material Hot-rolled to 0.5 In., Cold-rolled to 0.064 In. (87 Per Cent Reduction), Annealed at 450° C. One Series Cross-rolled and the Other Straight-rolled, Both Annealed One Hour at 800° C.

Amount of Reduction, Per Cent	Final Gauge, In.	Grain Size, Mm.	
		Reduction by Cross Rolling	Reduction by Straight Rolling
10	0.058	0.03	0.03
20	0.051	0.03	0.03
25	0.048	0.03	0.03
30	0.045	5–7, 0.03–0.04	0.02–0.03
40	0.038	10	0.03
50	0.032	5–7	0.03
60	0.026	10	0.03–0.04
70	0.019	5–7, 0.03–0.04	0.02–0.03
80	0.013	0.02–0.03	0.02–0.03
90	0.010	0.02–0.03	0.03–0.04

and confirm earlier results obtained in straight rolling, show the difference between the effect of cross and straight cold-rolling in the final stage, and indicate that large grains are developed on finally annealing at 800° C. with a cold-rolling reduction ranging between about 30 and 70 per cent. With reductions outside this range the final grain size is normal.

TABLE 8.—*Effect of Penultimate Annealing Temperature*

Material Hot-rolled to 0.5 In., Cold-rolled to 0.064 In. (87 Per Cent Reduction), Annealed at Temperatures Indicated, Cold-rolled to 0.032 In. (50 Per Cent Reduction) and Finally Annealed One Hour at 800° C.

Penultimate annealing temperature, deg. C.	150	200	250	300	350	400	450	500	550	600	650	700	725	750	775	800
Final grain size, mm.	0.03	0.03	10–12	15–17	15–17	17–20	20	10–12	10	5–7	5–7	5	5 and 0.04–0.05	0.04	0.04	0.04

Effect of Penultimate Annealing Temperature.—For determining the effect of the penultimate annealing temperature, samples cut from strip hot-broken down to 0.5 in. and cold-rolled to 0.064 in. were annealed for one hour at temperatures ranging up to 800° C. These materials were then cross-rolled with the usual 50 per cent reduction to 0.032-in. thickness and finally annealed at 800° C. The results of grain-size determina-

tions are given in Table 8, and show that for material finally cross-rolled there is a range of temperatures for the penultimate annealing operation that leads to the production of large crystals on finally annealing at 800° C. The optimum temperature appears to be of the order of 450° C., and from this temperature upward the final grain size gradually decreases until at 750° C. or more the grain size of the finished strip is normal.

Effect of Magnitude of Penultimate Rolling Reduction.—Just as the temperature of the penultimate annealing operation influences the formation of abnormally large grain size in finished sheet, so also do variations in the magnitude of the penultimate rolling reduction. Samples of hot-rolled copper at 0.50 in. were cold-rolled with reductions of 72 to 98 per cent, annealed at 450° C. for one hour, cold-rolled 50 per cent in thickness by cross rolling and finally annealed at 800° C. for one hour. The effect of the penultimate reduction on the final grain size is shown in Table 9.

TABLE 9.—*Effect of Penultimate Cold-rolling Reduction*

Material Hot-rolled to 0.5 In., Cold-rolled by Amounts Indicated, Annealed at 450° C., Cross-rolled with 50 Per Cent Reduction to Thickness Given in Second Column, and Finally Annealed One Hour at 800° C.

Penultimate Reduction, Per Cent	Penultimate Gauge, In.	Final Gauge, In.	Grain Size, Mm.
72	0.140	0.070	0.03
75	0.124	0.062	0.03
80	0.100	0.050	0.03
84	0.080	0.040	15–20, 0.03–0.04
85	0.075	0.0375	20–25
87	0.064	0.032	25–30
90	0.050	0.025	25
95	0.025	0.0125	0.02
98	0.010	0.005	0.02

The development of large grains occurs to a small extent with a penultimate rolling reduction of 84 per cent, and becomes more marked as the magnitude of the rolling reduction increases, until a maximum is reached at 85 to 90 per cent. With reductions of between 90 and 95 per cent, large crystals are no longer formed after the final annealing, and with reductions of 95 per cent and more the strip is fine grained. The large grains, therefore, are formed over only a small range of penultimate rolling reductions.

Confirming Experiments

The foregoing results indicate that the conditions giving rise to a large grain size are different, in respect of the final annealing temperature and the magnitude of the final rolling reduction, when the rolling is unidirec-

tional throughout and when the last rolling reduction is normal to the direction of previous rolling. Further experiments were made to ascertain the effect of annealing at 1000° C. material that had been finally cross-rolled with a reduction in thickness of 87 per cent, which is outside the range known to give the maximum grain size on annealing at 800° C. (Table 7). In order to obtain strictly comparable results and a check on the conclusions already reached regarding the conditions necessary for the production of abnormally large grain sizes, the experiment was extended to include observations on material that was finally cross-rolled and straight-rolled with reductions of two different magnitudes.

TABLE 10.—*Comparison between Straight and Cross Rolling at Final Reduction*

Material Hot-rolled to 0.5 In., Straight-rolled to 0.064 In. (87 Per Cent Reduction), Annealed at 450° C. and Finished to 0.032 In. (50 Per Cent Reduction) and 0.008 In. (87 Per Cent Reduction) by Straight and Cross Rolling, and Finally Annealed One Hour at Temperatures Indicated

Final Annealing Temperature, Deg. C.	Grain Size, Mm.			
	Cross-rolled		Straight-rolled	
	From 0.064 to 0.032 In.	From 0.064 to 0.008 In.	From 0.064 to 0.032 In.	From 0.064 to 0.008 In.
500	0.03	0.03	0.03	0.03–0.04
600	0.03	0.03–0.04	0.03	0.03–0.04
700	0.03	0.03	0.03	0.04
750	0.03–0.04	0.03	0.03–0.04	0.03–0.04
775	0.04 and 7	0.03–0.04	0.03–0.04	0.03–0.04
800	10–15	0.04	0.03–0.04	0.04
825	10–20	0.04	0.04	0.04
850	8–10	0.04	0.04–0.05	0.04–0.05
875	8–10	0.03–0.04	0.04–0.05	0.04
900	0.03–0.04 and 10	0.03–0.04	0.04	0.04
925	0.03–0.04 and 3	0.04	0.04–0.05	0.04–0.05
950	0.03–0.04 and 3	0.04–0.05	0.05–0.06	0.05
975	1.0	0.05–0.06	0.05–0.06	0.05–0.06
1000	0.5–1.0	*L*	1–2	*L*

A 0.45-in. thick hot-rolled O.R.C. copper strip was cold-rolled to 0.064 in. and annealed at 450° C. for one hour. From this thickness one portion was straight-rolled to 0.032 in. (50 per cent reduction) and another to 0.008 in. (87 per cent reduction). Further samples were cross-rolled to 0.032 and 0.008 in. These thicknesses correspond to total cold-rolling reductions from the original thickness, 0.45 in., of 92.9 and 98.2 per cent, respectively. All the samples at these two final thicknesses were annealed at temperatures varying from 500° to 1000° C. Complete grain-size results are given in Table 10.

When the results of straight and cross rolling are compared, it is seen that for 0.032-in. sheet the cross-rolled copper gives rise to large grains over the usual range, while, as expected, the straight-rolled strip does not produce any large grain sizes. The 0.008-in. strip behaves in a very similar manner whether straight-rolled or cross-rolled, developing an abnormally large crystal size at 1000° C. only. In both cases the crystals were of the same type; that is, the very large variety denoted by the letter *L*.

On contrasting the straight-rolled 0.008-in. strip with the cross-rolled 0.032-in. sheet, the outstanding difference in grain-size development is one of temperature. The 0.032-in. sheet develops large grains at 775° to 870° C., which thereafter decrease in size until at 1000° C. the structure, although coarse, is not abnormally large. There is no indication, however, of large grains in 0.008-in. strip at 800° C., and, in fact, they do not appear until the final annealing temperature reaches 1000° C.

In addition to confirming earlier findings, these results also show that with a very severe final cross rolling and a final annealing temperature of 1000° C. the large size of crystal formation is unlike that which results when the cross rolling is limited to about 50 per cent reduction and the maximum grain size occurs on finally annealing at about 800° C.

Hot-rolling Not Essential for Large Grain Size.—The material on which all the foregoing experiments have been carried out was initially hot-broken down, but that the initial hot-rolling process is not essential for the development of abnormally large grain sizes is shown by the following experiments.

A 0.850-in. thick piece of tough-pitch copper of H.C. (high conductivity) quality of the kind indicated by the figures for chemical composition given in the first column of Table 11 was cut from a 1000-lb. ingot of the dimensions already given, cold-rolled to a thickness of 0.500 in. and annealed at 550° to 600° C. The piece was cut into two halves, both of which were cold-rolled, one in the same direction as the previous rolling and the other in the cross direction, without any further annealing, both to a final thickness of 0.008 in., corresponding to a final cold-rolling reduction of 98.4 per cent. When finally annealed at 1000° C. for one hour, both strips developed large grains of the order of 40 to 60 millimeters.

Another piece of copper 1 in. thick was cut from a similar ingot and divided into two. One piece was cold-rolled without any intermediate annealing, down to a thickness of 0.025 in., which corresponds to a reduction of 97.5 per cent, and the resultant grain size was of the order of 0.05 to 0.06 mm. after annealing for one hour at 1000° C. The other piece was cold-rolled to a thickness of 0.850 in., annealed at 550° to 600° C., then cold-rolled to 0.025 in., which is equivalent to a final cold-rolling reduction of 97.05 per cent. After annealing for one hour at 1000° C., this material developed large crystals of the order of 40 to 60 millimeters.

These tests show, for this particular brand of tough-pitch H.C. copper, that a combination of heavy final cold-rolling and high final annealing temperature gives rise to the development of abnormally large crystals if the metal at its initial thickness prior to cold-rolling and annealing is either in the hot-rolled, or cold-rolled and annealed, condition, but not if it is in the cast state.

Effect of Composition.—All the results described were obtained on O.R.C. copper. Several different ingots were used in the course of the work, of the typical composition given in the first column of Table 11.

TABLE 11.—*Compositions of Coppers Investigated*

Percentages

Constituent	Varieties of Copper						
	O.R.C.[a]	C.C.C.[b]	Deoxidized	Oxygen-free	Braden Three Star Copper	Tough-pitch Arsenical	Deoxidized Arsenical
Copper	99.94	99.95	99.94	99.98	99.89	99.41	99.44
Oxygen	0.038	0.035	0.004		0.054	0.083	0.003
Tin		Slight tr.			tr.	0.005	0.005
Lead	Slight tr.	About 0.0005	Slight tr.	tr.	Less than 0.001	0.003	tr.
Iron	About 0.002	0.002	0.002	0.002	0.002	0.002	0.002
Nickel	Slight tr.		Slight tr.		About 0.02	0.05	0.07
Silver	0.002		0.002	0.002	0.005	0.006	0.006
Antimony		About 0.0003			0.0005	0.006	0.004
Bismuth		0.0001				0.0005	0.0005
Arsenic					0.001	0.42	0.40
Phosphorus			0.03				0.057

[a] Ontario Refining Company's electrolytically refined copper.
[b] Chile Copper Company's electrolytically refined copper.

The optimum conditions found necessary to produce, in this copper, large, irregular and striated crystals by heavy unidirectional cold-rolling followed by final annealing at 1000° C., and the somewhat smaller but still large and more equiaxed crystals, by a final cross rolling followed by annealing at 800° C., were applied to other varieties of copper, the compositions of which are given in the remaining columns of Table 11. With C.C.C. copper, similar results to those already described were obtained, except that the large crystals resulting from the cross-rolling treatment were somewhat smaller than those in the O.R.C. copper. With the two arsenical coppers and the deoxidized nonarsenical copper, no abnormally large crystals were obtained by either sequence of operations. Oxygen-free copper and the somewhat less pure fire-refined Braden 3 Star responded to the straight-rolling treatment and yielded large crystals

(Fig. 5), but by cross-rolling and annealing at 800° C. no large crystals were produced. It is, of course, possible that modifying the rolling and

Fig. 5.—Large crystals in oxygen-free copper after straight rolling. Natural size.

annealing conditions might produce large crystals in these coppers similar to those obtained with O.R.C. and C.C.C. copper.

Summary

Abnormally large crystal sizes can be developed in rolled copper strip or sheet provided the final cold-rolling reduction exceeds about 95 per cent

and the final annealing temperature is of the order of 1000° C. Similarly, large crystal structures can be produced under the same conditions of final annealing, with a final cold-rolling of not less than about 85 per cent, provided the temperature of the penultimate annealing does not exceed 550° C. and that the total cold-rolling exceeds 96 per cent. The structure after these heavy reductions is similar whether the final rolling is the same or normal to the direction of previous rolling.

If the final rolling reduction is limited to 30 to 70 per cent reduction, and is effected normal to the direction of previous rolling, the largest crystal size is obtained by annealing finally at about 800° to 850° C. The crystals are smaller than those obtained with heavier final rolling reductions followed by annealing at 1000° C., and differ from them in being much more equiaxed and free from circular markings and structures. For the production of these crystals by finally cross-rolling with a reduction of about 50 per cent and annealing at 800° to 850° C., the penultimate rolling reduction of about 90 per cent appears to be necessary, and the optimum annealing temperature prior to the final cross rolling is about 450° C.

These results have been obtained with two brands of H.C. copper, but with a phosphorus-deoxidized copper of comparable purity, except for the residual phosphorus, and less pure copper such as tough-pitch and deoxidized arsenical, large crystals were not produced by either sequence of operations.

Acknowledgments

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DISCUSSION

(D. K. Crampton presiding)

H. P. Croft,* Cleveland, Ohio (written discussion).—The authors have made a valuable contribution in regard to a problem that is of commercial as well as academic importance. We have encountered similar phenomena in electrolytic tough-pitch copper sheet that was annealed for 90 min. at 1150° F., rolled 45 per cent and annealed at 950° F. for 105 min. The final grain size was 0.020 mm. and the previous grain size 0.035 mm. Some of the material had grain sizes on the order of 0.500 mm. The exact previous history of this copper is unknown but this instance is cited merely to point out that this condition can occur at lower temperatures than those used in the authors' work.

We have also encountered similar large grain sizes in tubing fabricated under normal mill procedure. This has not been confined to tough-pitch copper alone but has also been found in copper with phosphorus contents varying from 0.010 to 0.020

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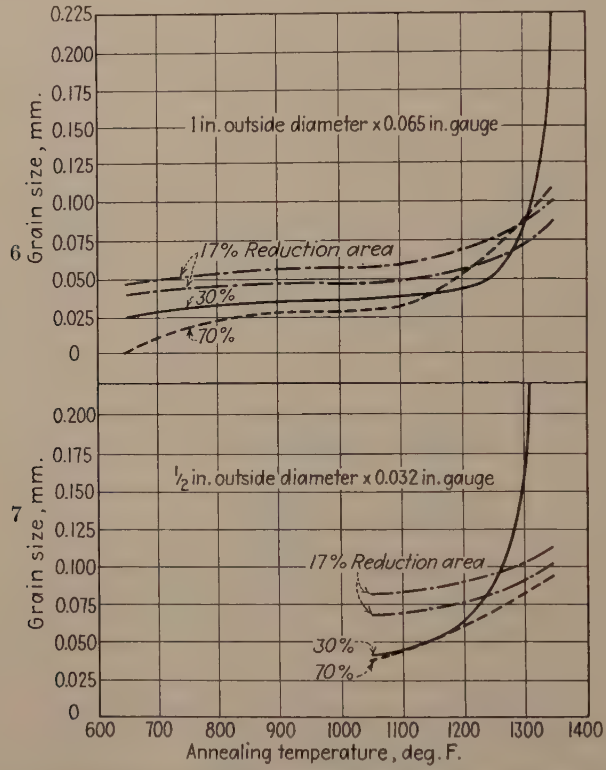
* Chief Metallurgist, Chase Brass & Copper Co., Inc.

per cent and temperatures ranging from 1000° to 1300° F. for the final annealing operation. Sometimes these large crystals occur in longitudinal streaks alternating in the same tube with parallel streaks of fine crystals and sometimes they occur in certain tubes of a given lot while the remainder of the load is normal. Alternate streaks of 0.025 mm. and 6.0 mm. have been found in the same tube. More of this condition is encountered in attempting to obtain grain sizes of 0.050 to 0.075 mm. on phosphorus-deoxidized tubing than with lower-temperature anneals but it is sometimes encountered in attempts to obtain 0.020-mm. grain sizes.



FIGS. 6 AND 7.—EFFECT OF PREVIOUS COLD-WORK ON GRAIN SIZE OF ANNEALED COPPER TUBING.

The type of crystals encountered are those illustrated in Fig. 5 but the grain sizes are of a lower order, ranging from approximately 0.300 to 6.0 mm. There is probably a condition of preferred orientation involved.

In an effort to investigate the cause of this condition we drew tubes from pierced billets of three different compositions:

1. Deoxidized copper containing 0.009 per cent P.
2. Deoxidized copper containing 0.019 per cent P.
3. Deoxidized copper containing 0.010 per cent P. and 0.008 per cent Ag.

These were given usual mill operations and anneals but finished with three different conditions, one tube of each composition being reduced 17 per cent to finish, the second tube reduced 30 per cent and a third tube reduced 70 per cent. Tubes of each composition finished with each type of reduction were then used as a basis for annealing

series, the anneals being carried out at 100° intervals between 650° and 1350° F. The results are shown in Fig. 6. Normal grain sizes were obtained with annealing, which followed reductions of 17 and 70 per cent, but the large grains developed on all three types of copper annealed at 1350° F., after a 30 per cent cold reduction in area. The results on the copper that was reduced 17 per cent are shown as a range instead of as a line because differences in grain sizes were apparent with the three types of copper following the light cold reduction. These differences disappeared with the heavier reductions.

Since these results did not follow previous theories on the subject, the experiment was repeated with three different billets from the same lots of copper, in this instance the tubes being drawn with the same reductions to ½ in. outside diameter and 0.032 in. gauge with the same temper draws. Similar results were obtained and shown in Fig. 7, the only noteworthy difference being that the large grains started to develop at even lower temperatures in the metal that had been reduced 30 per cent. It is noticeable that these results paralleled those given by the authors in Table 7, showing the grain size for cross-rolled sheet. It is quite possible that X-ray examination of the cross-rolled sheet and drawn tubing would show similar orientation for similar reductions.

This condition has been traced back in some specimens to the pierced shells where differences in grain size after hot piercing were noticed between the ridges and hollows resulting from the piercing operation. This work has not been carried out far enough to determine just when this phenomenon will occur and when it will be avoided. Certainly some other factors must enter into the problem, as the fact remains that certain tubes in a lot will develop this condition while others from the same batch of metal, handled as nearly in the same way as commercially possible, will not be subject to this excessive grain growth.

D. K. Crampton,* Waterbury, Conn. (written discussion).—The data given in this paper are particularly interesting in view of the fact that the conditions for formation of abnormal grains appear to be quite different from those generally considered to lead to such structures. For instance, we know that in most of the alpha brasses, at any rate, and in certain types of copper, abnormal grains are readily developed by a sequence of operations comprising: (1) an anneal of intermediate degree; (2) a rather light strain or cold-working; (3) a second anneal of about the same temperature as the first.

The abnormal grains developed by the present authors are exceptionally large but otherwise of the same general appearance as those formed by the sequence of operations referred to above. In other words, they are typified by very irregular or fragmented twinning bands and the presence of second-order and third-order twins. It seems obvious that even further studies of this interesting subject are desirable.

F. E. Carter,† Newark, N. J. (written discussion).—It seems to me that the authors have omitted a very important factor; namely, the thickness of the sheet. It has been my experience that the thickness of a sheet severely affects the apparent size of the grains, and, indeed, it seems logical to expect that if the grains in their natural three-dimensional growth tend to reach the surface, the latter should influence the grain size. In several of their tables, the authors show grain sizes greatly in excess of the thickness of the sheet and I feel that this condition may have been of greater influence than some of the factors enumerated in the paper. It would seem,

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* Director of Research, Chase Brass and Copper Co.

† Physical Metallurgist, Baker Platinum Works.

therefore, that reliable results can be obtained only when the final thickness of the sheet under investigation is much greater than the grain dimension.

W. H. Bassett, Jr.,* Hastings-on-Hudson, N. Y. (written discussion).—We should not overlook the fact that various grades of copper have different recrystallization temperatures. Small amounts of impurities in various commercial coppers have a definite effect on the recrystallization temperature. Some electrolytic coppers, for example, will recrystallize at temperatures from 50° to 100° F. lower than other electrolytic coppers. The question of the critical recrystallization temperature should be taken into consideration along with the previous history of the sample as regards the rolling schedule (number of passes and amount of reduction for each pass) when discussing the effect of time and temperature on the crystal growth of sheet copper.

M. Cook and C. Macquarie (written discussion).—As stated in the text, the paper is concerned with conditions giving rise to quite abnormal crystal sizes in rolled copper and not with crystal sizes that might be classified as coarse or large when judged by the standards used in referring to the structure of materials as normally produced. Thus, although a grain size of 0.500 mm., mentioned by Mr. Croft, is large or coarse by reference to normal grain sizes in rolled copper, it is not of the order of magnitude of the type of large crystals described in the paper, the dimensions of which can be measured in centimeters. In the course of our work we have noted the occurrence of grains of the order of 0.5 mm. in cross-rolled copper on annealing at 625° C. With copper similarly rolled, grains of the same order may occur at lower annealing temperatures if sufficient time is allowed for their formation. With deoxidized copper, containing 0.03 per cent P, we did not encounter, under any of the rolling and annealing conditions considered, a grain size in excess of 0.25 mm. It is of interest to note that Mr. Croft, with a reduction of 30 per cent on drawn copper tube, obtained an effect with regard to grain size similar to ours with cross-rolled sheet.

We did not obtain any large crystals in the course of the experiments that we made along the lines referred to by Dr. Crampton. An outstanding feature of the development of the type of abnormally large grains described in the paper is the relatively short annealing time required, and we agree with Dr. Crampton that this interesting subject merits further study.

Since the work is concerned with sheet metal and since the type of large crystals described are measurable in centimeters, it follows inevitably that their size is greatly in excess of the metal thickness. To do as Mr. Carter suggests would be scarcely practicable, for to finish at a thickness of 20 to 80 mm. would necessitate the commencement of rolling at a relatively very great thickness if the necessary reductions of the order of 90 per cent were to be given. In thicknesses that can be conveniently rolled under the required conditions the final gauge does not appear to have any effect on the formation of large crystals. Although many of the samples of straight-rolled large-grained copper produced were 0.008 in. thick, similar effects were obtained in sheet copper 0.025 in. thick, after annealing at 1000° C., by commencing with material sufficiently thick to obtain the necessary reduction.

With regard to Mr. Bassett's remarks, the annealing temperatures necessary for the development of the large grains described are so much greater than the recrystallization temperature of copper, which varies not only with the composition, as he states, but with other factors also, that it is not clear what connection there could be between recrystallization temperature and the formation of large grains. Their development would appear to be associated with structural influences brought about by certain combinations of deformation and subsequent annealing.

* Manager, Metallurgical Development, Anaconda Wire & Cable Co.

Plastic Deformation and Subsequent Recrystallization of Single Crystals of Alpha Brass

By M. R. Pickus,* Junior Member, and C. H. Mathewson,† Member A.I.M.E.

(Detroit Meeting, October, 1938)

The study of the plastic deformation and recrystallization of metals has been the subject of many investigations. In regard to the simple deformational processes, such as tension and compression, the early knowledge gained from studies of polycrystalline material has been supplemented by many significant researches on the behavior of single crystals. Unfortunately, this has not been true for more complicated deformational processes. As far back as 1927, G. I. Taylor[1] wrote:

> It is impossible in the present state of knowledge to do more than give a possible reason why (face-centered cubic) crystals set themselves with a (110) direction in the plane of rolling, and at right angles to the direction of rolling. The explanation of why the orientation of the crystal axes round the transverse direction is what it is, must be left till the distortion of metals, and particularly single crystals of metals in the process of rolling, has been studied in greater detail.

That this gap in the systematic study of deformation and recrystallization has not yet been filled was indicated by C. H. Samans,[2] who wrote in 1934 that "only four investigations upon cold-rolled single crystals of any of the face-centered cubic metals have been reported in the literature." Of these four studies, only those of S. Tanaka[3] and T. Sakao,[4] both of whom worked with aluminum crystals, had quantitative significance. The other two, carried out by F. Wever[5] and W. G. Burgers,[6] were of a qualitative nature.

It is our hope that the present investigation may contribute something to the knowledge necessary for a rationalization of the origin of rolling textures in terms of the known behavior of single crystals, and may add pertinent information concerning the recrystallization characteristics of deformed single crystals.

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* Graduate Student, Department of Metallurgy, Yale University, New Haven, Conn.

† Professor of Metallurgy, Yale University.

[1] References are at end of the paper.

Selection of Deformational Process

In view of the practical importance of the rolling process, it might appear desirable to study the effects of this type of deformation. It was felt, however, that the difficulty of rationalizing the rolling process from a crystallographic point of view constituted a disadvantage. After a consideration of the various possibilities, it was decided to use what Wever and Schmid[7] describe as a plane parallelepipedal compression. From our point of view this has the advantage of bearing a rather close resemblance to the rolling process, and at the same time is simpler to understand. This type of deformation causes a diminution in thickness of the specimen in the direction of compression, and an extension in only one direction; viz., at right angles to the compression axis, all lateral flow being prevented by the side walls of the device utilized to give this type of compression.

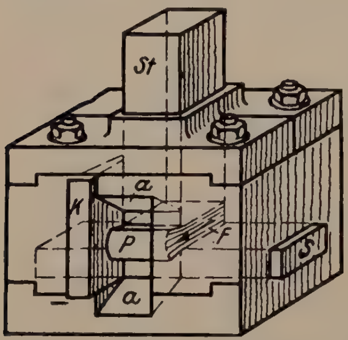

Fig. 1.—Device for plane parallelepipedal deformation (Wever and Schimd).

Fig. 1, due to Wever and Schmid, shows the construction of the mold, a description of which follows. The plunger *St* presses down on the specimen *P*, which is placed on a base plate and enclosed on three sides by steel walls so that the material can flow only in the direction *F*. The base plate was made in the form of a raised sill, *S*, to prevent any increase in the cross section of the specimen. The milled opening *a* assures an unrestricted flow of material. One of the side walls, *K*, was made in the form of a removable wedge, which facilitated the changing of specimens. The wedge *K* is locked in place by means of the sill *S*. If the direction of flow is visualized as the rolling direction, the similarity between the form change caused by plane parallelepipedal compression and that caused by rolling is apparent.

Preparation of Specimens

In this work it was decided to use an alpha brass containing nominally 70 per cent copper and 30 per cent zinc. Cartridge brass in the form of 1¼-in. rod was obtained through the courtesy of the Chase Brass and Copper Co., which gave the following analysis for the material: Cu, 70.24 per cent; Pb, 0.004; Fe, 0.01; Zn, remainder.

The single crystals were made by the Bridgman[8] method of gradual solidification of the metal from the molten condition. Cylindrical crystals about 8 in. long and 1½ in. in diameter were easily obtained by

this method. In order to remove coring, all of the crystals were given a high-temperature homogenizing anneal.

It is our belief that any account of work done on single crystals should be prefaced by a description of their degree of perfection in so far as it is possible to describe it. The production of true single crystals of alpha brass presents several difficulties. Obviously, the marked tendency of alpha brass to form twins excludes the use of the recrystallization method in making these large crystals. Consequently, the method of gradual solidification must be used. Greninger[9] has shown for copper that rapid rates of cooling favor the development of a pronounced macromosaic structure. Although this is an undesirable condition, it may be considered preferable to the use of very slow rates of cooling with consequent distillation of zinc over a prolonged period. Undoubtedly this would produce appreciable inhomogeneities. Consequently an intermediate rate of cooling was used. In practically every case the spots on X-ray films from these crystals showed some signs of a macromosaic structure, although usually in small degree. Just what effect a pronounced macromosaic structure would have on the mechanism of plastic deformation, we do not know. However, our results on these brass crystals have shown the general behavior that would be expected with single crystals of face-centered cubic metals.

The back-reflection Laue method of determining crystal orientations, as described by Greninger,[10] was used in this investigation. The crystal planes causing the spots on the X-ray films were identified by means of Greninger's hyperbolic net and a table of angles between important planes of the face-centered cubic lattice. Once the spots were identified, their angular coordinates were measured, and plotted on a stereographic projection in relation to the longitudinal axis of the crystal and the direction of the X-ray beam. When this projection was obtained, the points were rotated to bring a cube position to the center of the projection. Then it is a simple matter to locate the poles of all the important planes on the projection.

Since the specimens were to be in the form of rectangular parallelepipeds, the next step was to decide which crystal plane was to lie in the surface, and which crystal directions were to lie along the edges. When this decision was made, it was found expedient to rotate the points representing the longitudinal axis of the crystal, the direction of the X-ray beam, the pole of the plane that was to be parallel to the surface, and the direction that was to be parallel to an edge, so that the longitudinal axis fell at the center of the projection.

Suppose, for example, it was desired to cut a specimen having the plane (hkl) in the surface and the direction $[h'k'l']$ along an edge (assuming, of course, that the plane (hkl) contains the direction $[h'k'l']$). It is clear that the plane of the stereographic projection having the longitudinal

axis at the center actually represents a cross section of the specimen, as indicated in Fig. 2, I and II. In Fig. 2I, the point A is the reference mark placed on the crystal, which represents the direction of the X-ray beam; θ (IV) is the angle between the longitudinal axis L and the $[hkl]$ direction C that is to be the surface normal; ϕ is the azimuth of C in reference to the

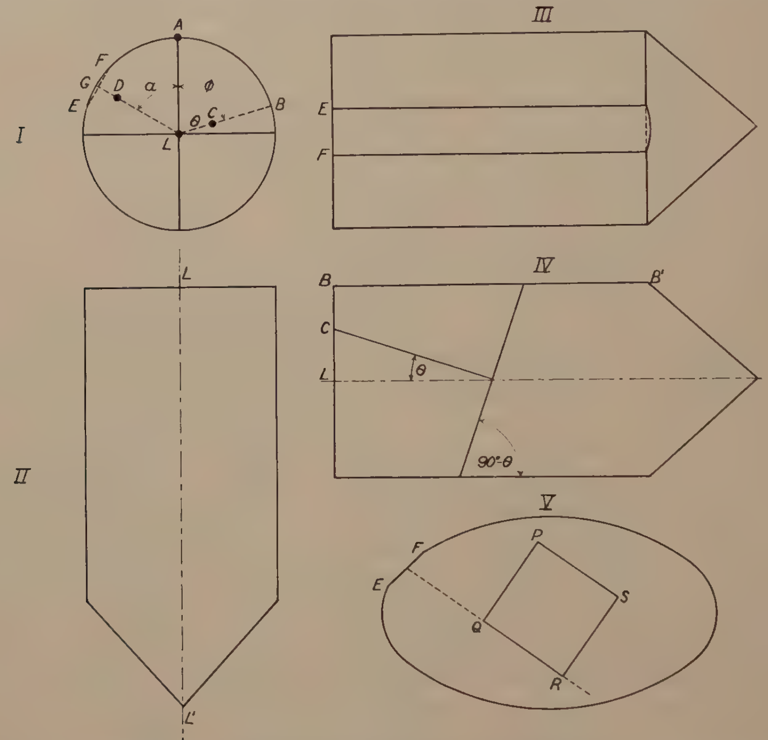

FIG. 2.—METHOD OF CUTTING OUT SPECIMENS.

I is a stereographic projection on which have been plotted the points L, A, C and D, of which L represents the longitudinal axis, A the direction of the X-ray beam, C the normal to the plane that is to lie in the surface, and D the direction that is to lie in the surface along an edge.

II indicates that the plane of the stereographic projection I represents a cross section of the crystal.

III shows the flat surface machined along GG'.

IV represents the plane through L, C and B of I, and indicates how to expose the required crystal plane, which is shown in V.

plane represented by LA; and α is the azimuth of the $[h'k'l']$ direction D that is to lie in the surface and along an edge. The lines LB and LG, making angles of ϕ and α, respectively, with LA, are drawn on the end of the crystal just as shown in Fig. 2I. From B the line BB' (IV) is drawn parallel to the longitudinal axis. A similar line GG' is drawn from G. Then a narrow, flat surface EF (Figs. 2I, III and V) is machined along GG'. Next a section making an angle of $(90° - \theta)$ with the longitudinal axis is cut as shown in Fig. 2IV. This exposes an (hkl) plane having an

elliptical contour as shown in Fig. 2V. Now a bevel protractor is placed along the flat surface EF so that its plane represents the plane LG (Fig. 2I) in which lies the $[h'k'l']$ direction D. The movable blade of the bevel protractor is rotated until it lies along the (hkl) plane that has just been exposed. A line drawn along the protractor blade represents the $[h'k'l']$ direction D, shown as QR in Fig. 2V; for this line satisfies the two conditions that it be an $[h'k'l']$ direction; it lies in the plane LG (Fig. 2I) and in the (hkl) plane shown in Fig. 2V. It is now a simple matter to cut the required parallelepiped, for we have located one surface and one edge, and all the surfaces and edges are mutually at right angles to one another. After the specimens were cut out, their orientations were checked by the X-ray technique previously described. The agreement was excellent, as the maximum error observed was never more than 2°.

Four specimens, ⅞ in. square (i.e., equal to cross section of plunger) and ½ in. high, were cut for each orientation. They were compressed in the mold described above to a reduction in thickness of 10, 20, 30 and 60 per cent, respectively. It was found that in order to obtain a homogeneous deformation, friction had to be kept as low as possible. Toward this end, the side walls, the end of the plunger, and the top of the base plate were given a high polish. In addition the specimens were lubricated with a mixture of castor oil and graphite as suggested by Wever and Schmid.

Selection of Orientations

A complete determination of the influence of orientation on the properties of crystals that have been subjected to a given deformation requires the use of a large number of specimens. The usual procedure, in the case of tension or compression, is to choose orientations so that the various regions of a stereographic triangle, whose three corners are the poles of cube, octahedral and dodecahedral planes, respectively, are well represented. The use of deformational processes of lower symmetry complicates the situation considerably. Instead of a single axis, as in tension and compression, two axes must be employed to describe the type of deformation used in this work; viz., one parallel to the direction of compression and one parallel to the direction of flow. For each position of the compression axis there is an infinite number of possible positions for the direction of flow, the locus of which, in terms of a stereographic projection, is the great circle 90° from the compression axis. Evidently there is a twofold infinity of possibilities. Consequently an attempt was made to find a rational basis on which to classify the various possible orientations. After careful consideration, it seemed logical to divide the possibilities into two general categories. Orientations for which the compression axis and the direction of flow occupied positions of crystallographic symmetry constituted one class, while the other class contained

those orientations for which the deformational axes occupied unsymmetrical positions. It seemed reasonable to suppose that these two types of orientations might show a maximum difference in properties. On this basis five sets of specimens were prepared, the orientations of which are shown in Fig. 3, where C indicates the axis of compression and F, the direction of flow. For convenience in referring to the various specimens, a nomenclature has been adopted, which may be explained by considering a specific case. S4-30 is a single crystal specimen, whose orientation is that of set 4 and which has been subjected to a reduction in thickness of nominally 30 per cent.

A study of the recrystallization of all five sets of specimens was made. In addition, an X-ray investigation of the orientational changes in sets S4 and S5 was carried out. The X-ray analysis was confined to two sets because of time limitation. The reasons for choosing the orientations S4 and S5 are indicated in the following paragraph.

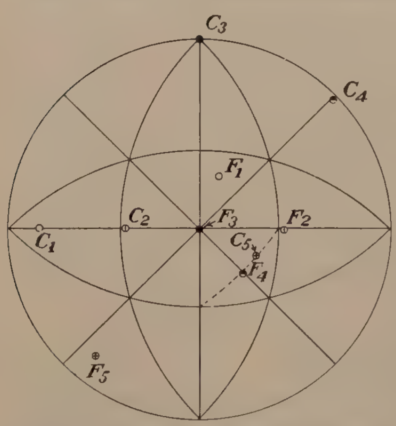

FIG. 3.—ORIGINAL ORIENTATIONS OF THE FIVE SETS OF SINGLE-CRYSTAL SPECIMENS.

It is a well established fact that when polycrystalline aggregates of the face-centered cubic metals are cold-rolled, a reorientation process sets in, which leads to certain preferred crystallographic positions for the deformation axes. The end position most frequently reported has a {110} plane parallel to the surface and a <112> direction parallel to the rolling direction. Many attempts have been made to rationalize this behavior in terms of the known characteristics of single crystals, but it is generally conceded that none of the proposed explanations is entirely satisfactory. This subject is treated from a theoretical point of view elsewhere.[11] It is a principal purpose here to describe experiments carried out in an attempt to ascertain whether the end position $(1\bar{1}0)$, [112] is significant for single crystals as well as for polycrystalline aggregates. From Fig. 3 it may be seen that the orientation of S4 corresponds to the end position $(1\bar{1}0)$, [112]. Hence it might be expected that S4 would show a maximum stability, in the sense that no change in orientation should occur. The orientation of S5, on the other hand, was expected to show a minimum stability, since each of the deformation axes occupied positions of low crystallographic symmetry, within the stereographic triangles.

RESULTS OF X-RAY INVESTIGATION

The orientations of the specimens were determined at various stages of the deformation. Up to reductions in thickness of 30 per cent, the

back-reflection Laue method of determining orientations was quite satisfactory. The results are shown stereographically in Figs. 4 and 5.

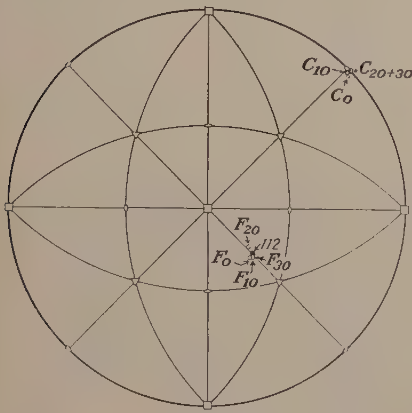

FIG. 4.

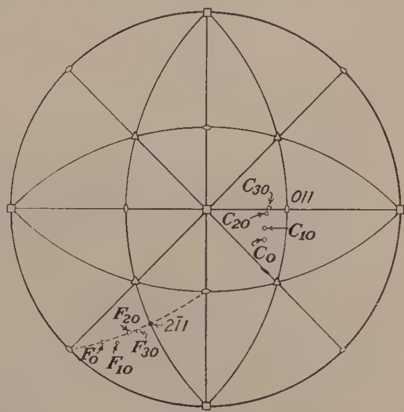

FIG. 5.

FIG. 4.—ORIENTATION CHANGES OF S4.

Direction of flow is designated by F and the compression axis by C. Subscripts refer to the percentage reduction in thickness.

FIG. 5.—ORIENTATION CHANGES OF S5.

Direction of flow is designated by F and the compression axis by C. Subscripts refer to the percentage of reduction in thickness.

Fig. 4 shows very definitely that when the initial orientation has the compression plane parallel to a $(1\bar{1}0)$ plane and the direction of flow parallel to a [112] direction, no change in orientation occurs. Even when the deformation axes occupy positions of very low symmetry, as in S5 (Fig. 5) there is a tendency for a rotation to occur so that this favored orientation $(1\bar{1}0)$, [112] is approached. It is felt that these results are quite conclusive evidence that the orientation $(1\bar{1}0)$, [112] has great significance in connection with single crystals, as it has for polycrystalline aggregates.*

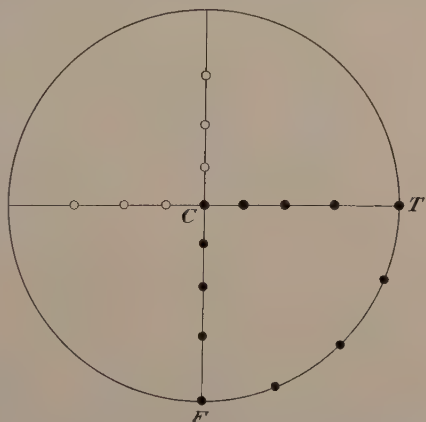

FIG. 6.—STEREOGRAPHIC PROJECTION OF VARIOUS POSITIONS OF X-RAY BEAM RELATIVE TO SPECIMEN USED IN WORKING OUT POLE FIGURES.

The analysis of the specimens that were reduced 60 per cent was more difficult. For such high degrees of deformation a single X-ray pattern does not suffice. However, the use of pole-figure methods such as those described by W. E. Schmid[12] permits a very complete description of the orientational relationships existing in severely deformed material. The usual procedure is to allow a monochromatic X-ray beam to pass through

* This, of course, does not exclude other orientational end points in special cases.

a thin section of the material, which is placed between the film and the slit system. In the present work the specimens were to be used for a subsequent recrystallization study, and hence could not be sectioned for this purpose. Therefore, a back-reflection procedure was developed. Both the transmission method and the back-reflection method have their own peculiar advantages and disadvantages. The transmission method requires a long, tedious grinding operation, and usually long exposures

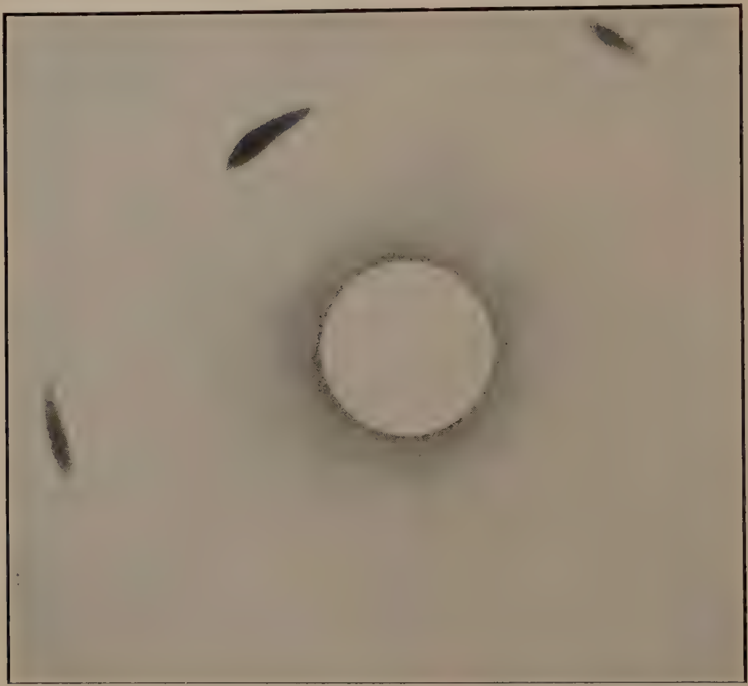

FIG. 7.—DIFFRACTION PATTERN OF SINGLE CRYSTAL (S4-60) OF ALPHA BRASS, REDUCED 60 PER CENT IN THICKNESS BY PLANE PARALLELEPIPEDAL COMPRESSION.

X-ray beam was parallel to compression axis. Inner ring corresponds to a (222) reflection, and outer ring to a (113) reflection.

are necessary. The back-reflection method requires no grinding and relatively short exposures—one hour in the present work. However, the reflection circles in the latter case are comparatively small, consequently a few more exposures are required to completely cover the projection circle. It may be pointed out here that caution must be exercised in the interpretation of results obtained by either method. Thus, it is possible that the texture varies from the interior to the exterior of the specimen. Schmid and Wassermann,[13] and Edmunds and Fuller[14] have shown this to be true for cold-rolled zinc sheet. A similar situation was found for aluminum sheet by v. Vargha and Wassermann.[15]

In the present work all of the specimens to be X-rayed were carefully machined to a sufficient depth to remove any surface effects. They were

then polished and given a deep etch. Strictly speaking, the resulting pole figures must be applied only with relation to the material in the vicinity of this final surface. However, other considerations seem to indicate that a fairly uniform condition existed in the specimens. Each specimen was continuously moved in a plane parallel to itself during the exposure, which gave a reflection integrated over an appreciable area. The fact that all of the integrated reflections obtained from three surfaces

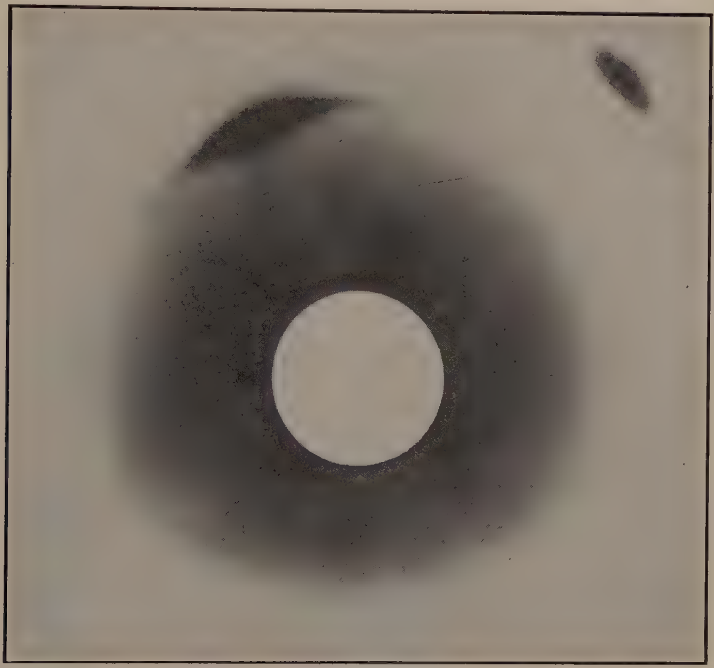

FIG. 8.—DIFFRACTION PATTERN OF SINGLE CRYSTAL (S5-60) OF ALPHA BRASS, REDUCED 60 PER CENT IN THICKNESS BY PLANE PARALLELEPIPEDAL COMPRESSION.

X-ray beam was parallel to compression axis. Inner ring corresponds to a (222) reflection, and outer ring to a (113) reflection. The similarity between the (222) reflections for S4-60 and S5-60 is apparent.

mutually perpendicular presented a consistent relationship indicates that the deformation must have been fairly homogeneous.

Eighteen exposures were taken for each specimen. The positions of the X-ray beam (FeKα radiation) relative to the specimen are shown stereographically in Fig. 6, in which the letters C, F and T refer to the compression axis, the direction of flow, and the transverse direction, respectively. The pole figures were first worked out on the basis of the reflections for which the positions of the X-ray beam are shown by the black circles. The positions indicated by the white circles were included to provide a check and to reduce the possibility of missing any important coverages. Two of the X-ray patterns are shown in Figs. 7 and 8, and the pole figures for S4-60, and S5-60 are given in Figs. 9 and 10, respectively.

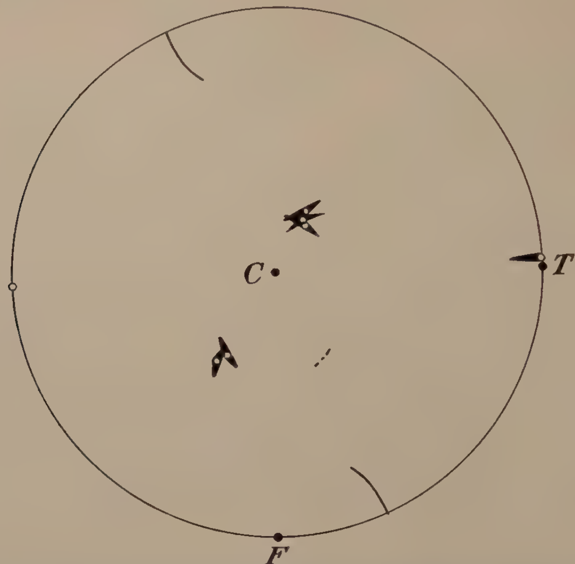

FIG. 9.—POLE FIGURE FOR (222) PLANES OF SINGLE CRYSTAL (S4-60) OF ALPHA BRASS REDUCED 60 PER CENT IN THICKNESS BY PLANE PARALLELEPIPEDAL COMPRESSION.

F, *C* and *T* refer to direction of flow, the compression axis and the transverse direction, respectively.

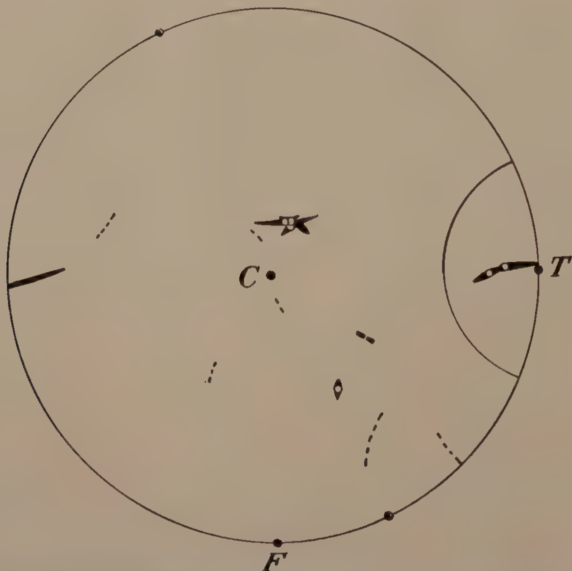

FIG. 10.—POLE FIGURE FOR (222) PLANES OF SINGLE CRYSTAL (S5-60) OF ALPHA BRASS REDUCED 60 PER CENT IN THICKNESS BY PLANE PARALLELEPIPEDAL COMPRESSION.

F, *C* and *T* refer to direction of flow, the compression axis and the transverse direction, respectively.

Several methods may be used in the interpretation of pole figures, and in this instance a very simple expedient was employed. Fig. 11 shows the distribution of {111} poles in an ideal pole figure having a {110} position at the center of the projection. If we compare Figs. 9 and 11 and imagine that C corresponds to a $[1\bar{1}0]$ and F to a [112] direction, we see that there is a remarkable resemblance between the two figures (the small white circle on the periphery of Fig. 9 represents a localized region of maximum intensity). Another striking feature of Fig. 9 is the small degree of

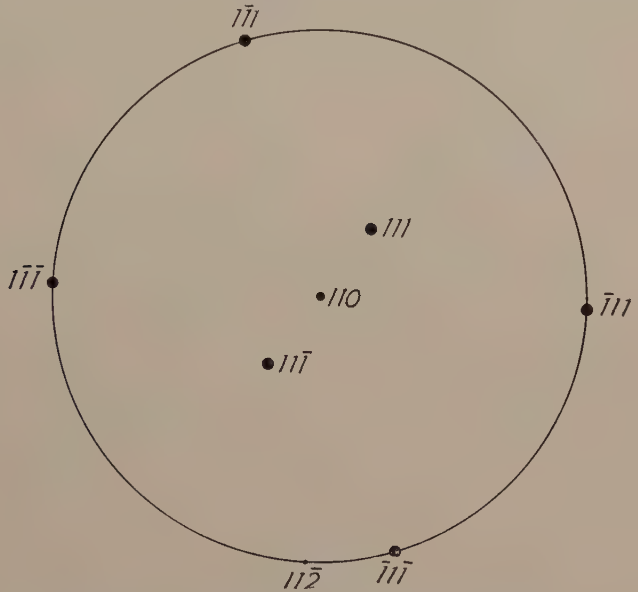

FIG. 11.—DISTRIBUTION OF {111} POLES IN AN IDEAL POLE FIGURE (FACE-CENTERED CUBIC LATTICE) HAVING {110} POLE AT CENTER.

scattering. With the exception of the region indicated by a dotted curve below and to the right of C, no coverages other than those corresponding to the ideal pole figure were found, and it will be seen later that this weak coverage has an interesting implication. This pole figure proves rather definitely that S4 has shown no tendency to change its original orientation even after a 60 per cent reduction.

Even though the original orientation of S5 was so different from that of S4, comparison of Fig. 10 with Fig. 9 shows that the two pole figures are very similar. In this case, however, there is considerably more scattering, although it should be pointed out that the broken curves indicate regions of rather low intensity. The regions of maximum intensity correspond rather well with those of the ideal pole figure (Fig. 11). It is interesting to notice that in both Figs. 9 and 10 there are two regions below C that are somewhat similarly arranged but are in the reverse order with respect to intensity. It may be seen also that to the right of F and on the

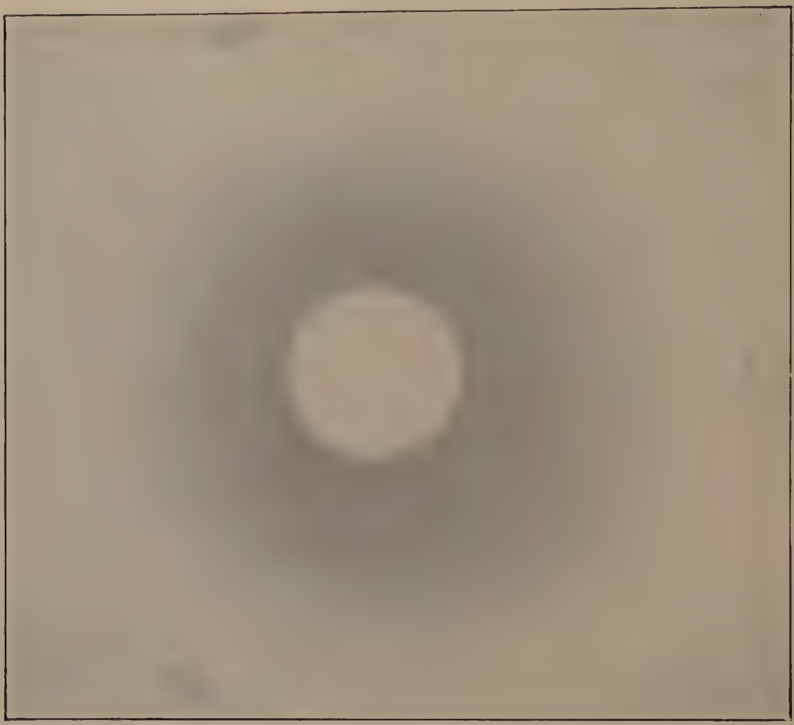

FIG. 12.—DIFFRACTION PATTERN OBTAINED WITH X-RAY BEAM NEARLY COINCIDING WITH AN OCTAHEDRAL COVERAGE. TRIGONAL SYMMETRY IS CLEARLY SHOWN.

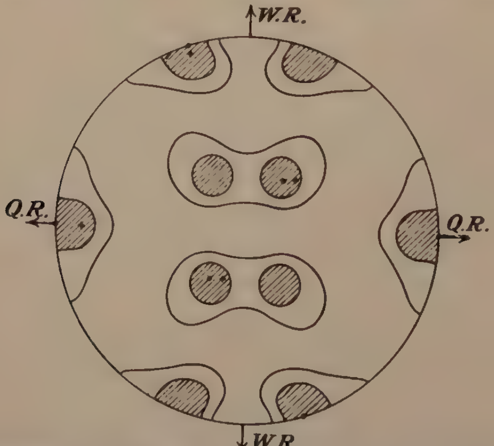

FIG. 13.—POLE FIGURE FOR OCTAHEDRAL PLANES (111) OF COLD-ROLLED POLYCRYSTALLINE ALPHA BRASS (85 PER CENT CU) (V. GÖLER AND SACHS).

periphery of the projection circle there occurs an octahedral coverage in both cases. This circumstance permitted an excellent check on the interpretation of these results. If the key to exposures for pole figures (Fig. 6) is now considered, it will be seen that there is a black circle on the periphery just to the right of *F*. This position coincides almost exactly

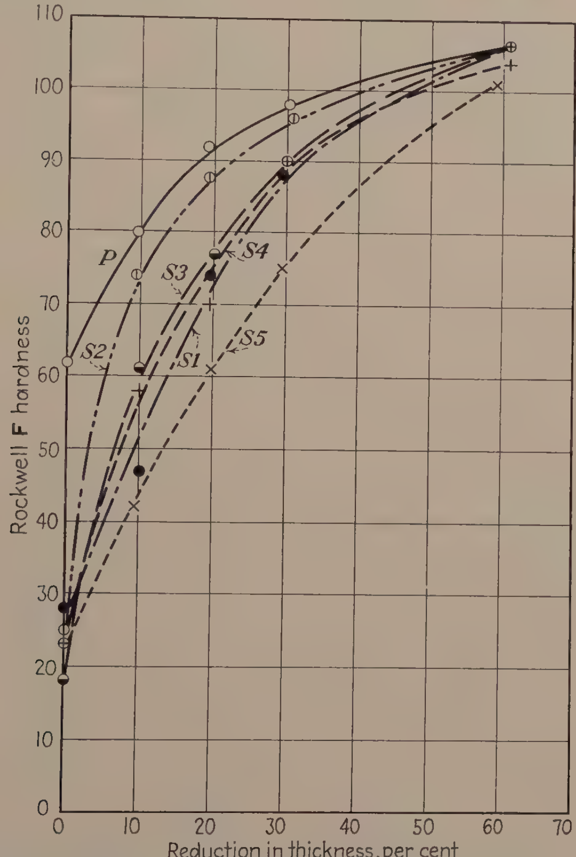

FIG. 14.—CURVES SHOWING ROCKWELL HARDNESS AS A FUNCTION OF DEGREE OF DEFORMATION.

with the two coverages under consideration. Therefore the patterns obtained with the X-ray beam in this position should show definite trigonal symmetry for both S4 and S5, and this was found to be true. One of the patterns is shown in Fig. 12.

It is instructive to compare Figs. 9 to 11 with Fig. 13 due to v. Göler and Sachs,[16] which is a pole figure obtained from cold-rolled polycrystalline brass (85 per cent Cu). The simple orientation of Fig. 11 accounts for half the number of coverages of Fig. 13. If the poles of Fig. 11 are rotated 180° about the line containing the {110} and {112} positions, the

other half are accounted for. Apparently the polycrystal texture consists of these two orientations superimposed on one another. There must also have been some tendency for the single-crystal specimens to develop this dual relationship. This would explain the region of weak intensity in Fig. 9, and may also account for the rather intense region below and to the right of C in Fig. 10. With regard to Fig. 10, it should be pointed out that, in general, a deformation of 60 per cent is hardly sufficient to effect a sharp adjustment in the development of a texture. In summation, it seems that practically all of the coverages found for the two single-

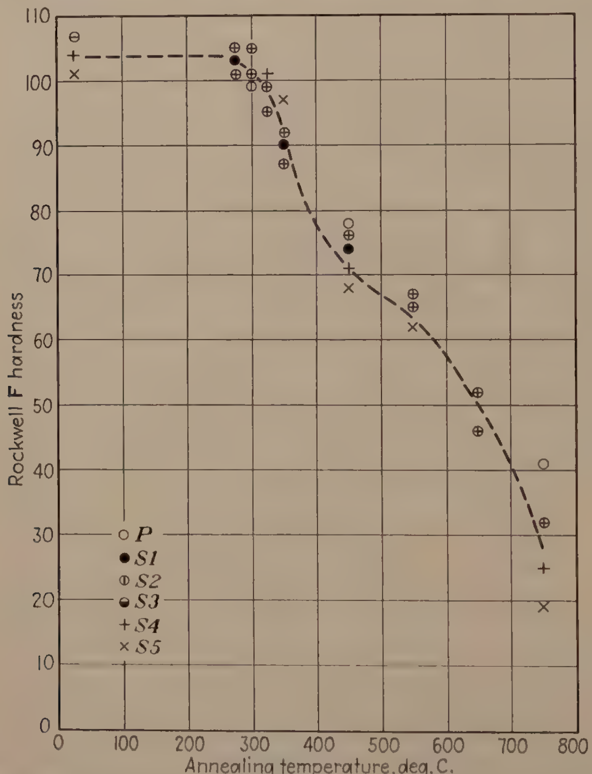

FIG. 15.—RECRYSTALLIZATION CURVE FOR REDUCTION IN THICKNESS OF 60 PER CENT.

crystal specimens, despite their differences in initial orientation, are well accounted for by the pole figure from a polycrystalline aggregate.

The orientation studies just described furnish an illustration of the well-known fact that the evidence from a single X-ray pattern of a cold-worked material may be very misleading. Thus, when the X-ray beam was parallel to the transverse direction of S5 (Fig. 10), practically the complete Debye-Scherrer ring was obtained on the film, which might be taken to indicate that substantially random orientations exist in the specimen. However, when the X-ray beam was directed along the

compression axis C, indications of a very marked preferred orientation were obtained as illustrated by Fig. 8.

Recrystallization Studies

Rockwell F hardness readings were taken on each specimen of the five sets of single crystals. One specimen of each set was then compressed in the mold described on page 162 to a reduction in thickness of 10, 20, 30 and 60 per cent, respectively. After the deformation, the hardness was again recorded. Each specimen was then annealed for

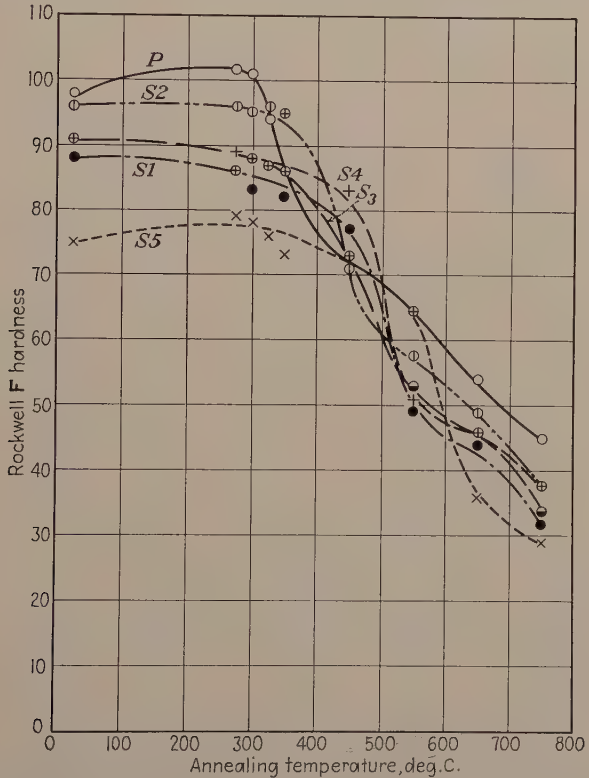

Fig. 16.—Recrystallization curves for reduction in thickness of 30 per cent

½ hr. at each of the following temperatures: 275°, 300°, 325°, 350°, 450°, 550°, 650° and 750° C. Hardness values were obtained after each anneal. For the sake of comparison a set of polycrystalline specimens was given exactly the same treatment. This set is designated by the letter P.

In order to facilitate a comparison between the behavior of the polycrystalline specimens and the different sets of single crystals, the recrystallization data on all specimens for the same degree of deformation have been grouped together in Figs. 14 to 16.

The configuration of the curves representing these recrystallization data seemed rather unusual, as the hardness, especially in connection with the 60 per cent deformation, decreased almost as rapidly beyond the temperature range of expected recrystallization as during the period of recrystallization. Several possible explanations of this were apparent. It will be recalled that in this work each specimen was heated at every temperature in the annealing schedule. It thus appeared possible that the rather sharp drop in hardness accompanying a given rise in temperature, in a range well above the recrystallization temperature, might be a manifestation of some peculiar cumulative effect in the annealing process. On the other hand, it was suspected that the trend of the curves might be due to a characteristic inherent in the Rockwell F scale. Again, it could be imagined that recrystallization subsequent to the particular type of deformation process used in this work might proceed in some unique manner. In order to investigate these possibilities the following experiment was undertaken.

A short length of the cold-drawn brass rod used in the original investigation was first annealed for ½ hr. at 650° C., then cold-rolled to a reduction in thickness of 59.8 per cent. From this bar 16 specimens 1½ by 1 by ½ in. were cut and numbered. Specimens 1 and 9 to 15 were heated for ½ hr. at 275° C. Then specimens 9 to 15 were taken through the annealing schedule, using the "cumulative" anneal; i.e., the specimen corresponding to an anneal at some particular temperature was also annealed at each of the lower temperatures in the schedule. At the same time specimens 2 to 8 were given a "normal" anneal; i.e., each specimen was annealed at only one temperature. Specimen 16 was left in the cold-rolled condition. When the annealing program was completed, both the Rockwell F and the Brinell hardness of each specimen was determined. This experiment gave simultaneously a comparison of the Rockwell F scale with the Brinell hardness numbers obtained with a 500-kg. load applied for 60 sec., and also a comparison of the "cumulative" anneal with the "normal" anneal.

The results are shown graphically in Figs. 17 and 18. Here, the points representing the cumulative anneal are represented by black circles, and a coincidence of the points obtained by the two methods of annealing is indicated by half blackened circles. It appears from these curves that for all temperatures except those in the range 275° to 325° C. the points obtained by using the "cumulative" anneal coincide with those obtained by using the "normal" anneal. Even in the range 275° to 325° C. the discrepancy is small. A comparison of these curves with those shown in Figs. 15 and 16 demonstrates clearly that the peculiar character of the original curves is due to properties inherent in the Rockwell F scale.

Discussion of Recrystallization Data

A precise explanation of the differences between the various curves of Figs. 14 to 16 would require a rather thorough understanding of the crystallographic mechanism of the deformation process in each case. From a theoretical point of view, the percentage reduction in thickness presents a somewhat arbitrary basis for comparison. Preferably, one should discuss the deformation in terms of the amount of shear resolved along the participating slip systems, as is customary in dealing with the extension and compression of single crystals. In the more complex

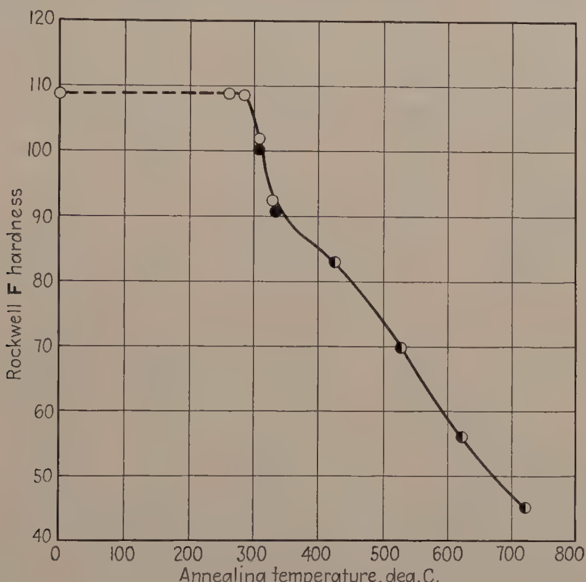

Fig. 17.—Rockwell F hardness as a function of the annealing temperature for alpha brass (polycrystalline) cold-rolled to a reduction in thickness of 59.8 per cent.

deformational processes, such as the type used in the present investigation, however, very little is known with any degree of certainty concerning the slip mechanisms involved. In the general case, even if a probable set of operating slip systems were selected on the basis of certain assumptions, there would still remain the problem of deciding the relative amounts of shear along the various systems. Therefore, until more information is available it seems necessary to express the extent of the deformation in terms of the percentage reduction in thickness. Consequently, it is felt that anything beyond a limited discussion of these curves must await the development of a more comprehensive point of view.

Subject to these limitations, then, the following comments are offered. Fig. 15 indicates that for reductions in thickness of 60 per cent or greater

the recrystallization temperature is practically independent of the initial orientation; in fact, very similar to that of polycrystalline metal. Moreover, the curves of Fig. 14 show that the hardness values of all the specimens after a 60 per cent reduction differ but slightly from one another. This might be construed to imply that the fragmentation at these high reductions is so great that material that was initially a single crystal has become essentially polycrystalline, and that therefore these specimens would be expected to exhibit similar recrystallization characteristics. However, the results of the X-ray investigation suggest

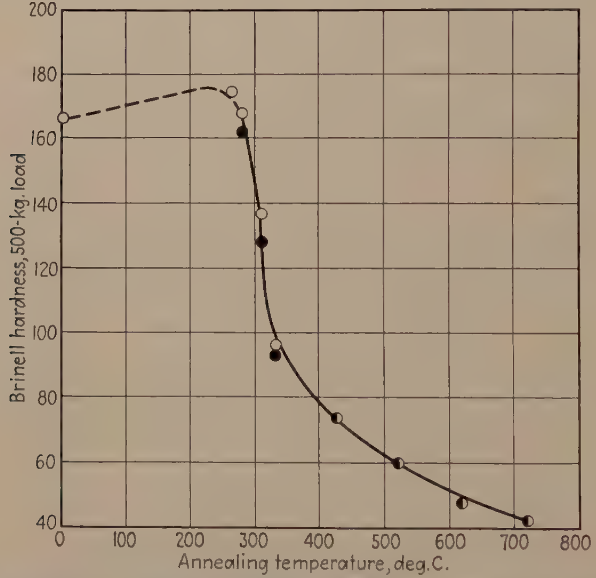

FIG. 18.—BRINELL HARDNESS NUMBERS (500-KG. LOAD APPLIED FOR 60 SEC.) AS A FUNCTION OF THE ANNEALING TEMPERATURE FOR ALPHA BRASS (POLYCRYSTALLINE) COLD-ROLLED TO A REDUCTION IN THICKNESS OF 59.8 PER CENT.

another factor that may be instrumental in causing the specimens having a 60 per cent reduction to recrystallize similarly. This is the indication that single crystals may develop the same type of preferred orientations as those shown by polycrystalline metal when subjected to severe working. If the crystallographic mechanism of the deformation towards the latter stages is similar whether the material was originally a single crystal or a polycrystalline aggregate, it should not be surprising to find the recrystallization process similar in all cases.

The curves for the lower reductions* indicate a dependence of recrystallization temperature on orientation. Inasmuch as Fig. 14 shows that the hardness developed after a given amount of reduction is dependent

* Only the curves for a 30 per cent reduction are presented here, since they are typical of the results obtained for intermediate degrees of deformation.

on the initial orientation, it seems pertinent to inquire whether all of the single-crystal specimens, regardless of initial orientation, would show the same recrystallization temperature if they were subjected to the varying amounts of deformation necessary to produce the same degree of hardness. In order to clarify this point, Fig. 19 was derived from the recrystallization data. The recrystallization temperature was taken to be the temperature at which the first inflection point occurs in the recrystallization curve. The fact that the nine points, representing five different orientations, lie approximately on a smooth curve suggests that

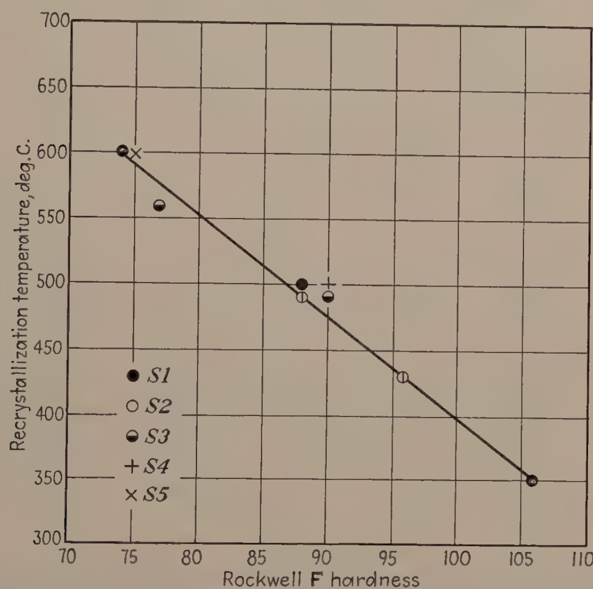

FIG. 19.—RECRYSTALLIZATION TEMPERATURE AS FUNCTION OF HARDNESS FOR SINGLE CRYSTALS OF VARIOUS ORIENTATIONS.

under the conditions of these experiments the recrystallization temperature is determined primarily by the degree of hardness attained in the working process. No particular significance is attached to the fact that in Fig. 19 the data are represented approximately by a straight line. This is merely a characteristic of the Rockwell F scale. If Brinell hardness is plotted instead of Rockwell hardness, the points fall on a curve, which, though still smooth, has an appreciable curvature.

No unified and consistent interpretation of data pertaining to the association of hardness with recrystallization can be given at the present time. Polanyi and Schmid[17] and Czochralski[18] found in their work on single crystals of tin and aluminum, respectively, that hardening is not directly associated with recrystallization. In the portions of the specimens where bending of the lamellae was most pronounced, recrystallization took place preferentially. If the lamellae were restraightened,

even though the hardness was increased, recrystallization did not occur. Van Arkel and his co-workers,[19,20] who worked with polycrystalline metals, on the other hand, have described evidence pointing to the existence of a direct relationship between hardening and recrystallization. Beck,[21] in summarizing his own results, concludes that "there is no direct physical relationship between hardening and recrystallization."

In view of this diversity of opinion, it should be emphasized that a relationship such as the one shown in Fig. 19 is of necessity an approximation, and is applicable only under conditions similar to those obtaining in the present experiments.

In conclusion it may be noted that the hardness curves of Fig. 14 have been considered from a theoretical point of view elsewhere,[11] in a more general discussion of the origin of rolling textures.

Summary and Conclusions

1. A method was described for cutting rectangular parallelepipedal specimens, having a definite crystallographic orientation, from large cylindrical crystals. The procedure, which was based on X-ray measurements (back-reflection Laue method), gave accurate results.

2. The recrystallization process subsequent to various degrees of plane parallelepipedal compression was investigated. The results indicate that for intermediate degrees of deformation single crystals require a higher temperature to effect recrystallization, and recrystallize over a wider range of temperature than does polycrystalline material. For reductions in thickness of 60 per cent or more, the recrystallization temperature appears to be independent of the orientation of single crystals; in fact, practically no difference was observed between the single crystal and the polycrystalline specimens.

3. An X-ray investigation of the orientation changes accompanying the deformation was made. The results prove definitely that the orientation $(1\bar{1}0),[112]$ is significant for single crystals, as with polycrystalline material, and suggest that the development of textures is probably due to a similar mechanism in both cases.

Acknowledgments

The authors desire to acknowledge their indebtedness to Mr. H. L. Burghoff, Prof. Arthur Phillips and Prof. L. W. McKeehan, for constructive criticism, and to the Chase Brass and Copper Co. for material used in the investigation.

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DISCUSSION

(Robert F. Mehl presiding)

P. A. Beck,* Barber, N. J. (written discussion).—One of the many very interesting results of this work is that the temperature of recrystallization, as a function of the hardness, is invariant with respect to the initial orientation of the compressed brass single crystals. I would like to join the authors in their statement that such a relationship is of necessity only applicable under conditions similar to those obtaining in the present work. The "hardening rule" of Van Arkel is also valid under analogous

* Central Research Laboratory, American Smelting and Refining Co.

restriction only. This rule states that in stretched polycrystalline aluminum strips the grain size of the recrystallized material, as a function of the hardening, is invariant with respect to the initial grain size of the strips.

These relationships, obtaining under certain well-defined conditions, do not involve any contradiction to the fact that hardening has no direct physical relation to recrystallization. The situation here is somewhat similar to that of a gas under compression, where there is no physical relation between the volume and the pressure. However, such a relation is established if the conditions of the compression process are defined (e.g., adiabatic, or isothermic, or the like). Similarly, a certain hardness value may be realized by various deformation processes, leading to different recrystallization properties, but a one to one correlation between hardness and recrystallization properties is established if the conditions of the deformation process are defined.

Consequently, it seems to me that the apparently divergent views of the various authors quoted in the paper are not really antagonistic. Each one depicts a part of the truth, and they can be reconciled with each other just as well as can the phenomena they truthfully describe.

C. S. Smith,* Waterbury, Conn. (written discussion).—The authors show a step in the hardness curve resulting from annealing severely deformed alpha brass at progressively increasing temperatures, and suggest that it results from a peculiarity of the Rockwell test. I do not think that this is so, for, although the Rockwell hardness numbers lie on anything but a linear scale in relation to any reasonable index of true hardness, there is no reversed behavior in the middle of the range but only a progressively decreasing sensitivity as the hardness numbers become higher. The Brinell test gives a more linear scale and would not show the step in the curve to such a degree just because it is proportionally (not absolutely) less sensitive than the Rockwell test on this particular material.

The true explanation, to my mind, lies in the fact that after recrystallization to a small grain size had occurred at the usual temperature, further grain growth was inhibited by the presence of inclusions or some precipitated material and that at a higher temperature these inclusions coalesced or dissolved and allowed normal grain growth and softening to occur. Common brass with appreciable iron content behaves in much this way, and, indeed, one can almost plot the change of solubility of iron in brass by noting the temperature at which grain size and hardness become normal for brasses of different iron contents.

C. S. Barrett,† Pittsburgh, Pa. (written discussion).—It is pleasant to see how well deformation textures can be explained by single-crystal behavior, both in the deformation of a face-centered cubic alloy in this research and in the compression of body-centered cubic iron reported by the writer at this meeting.[22] Studies of the deformation of iron by rolling, which Dr. Gensamer and I are now carrying out, are also showing a good correlation between single-crystal and polycrystal behavior, and Mr. Levenson and I are finding a similar correlation between single crystals and polycrystals in the texture of iron wires. It is not unlikely that all deformation textures will soon be found to be entirely consistent with single-crystal behavior, particularly when the single crystals are deformed in a manner consistent with their deformation in the aggregate.

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* Research Laboratory, American Brass Co.

† Physicist, Metals Research Laboratory, Carnegie Institute of Technology.

[22] C. S. Barrett: The Structure of Iron after Compression. A.I.M.E. *Tech. Pub.* 977 (*Metals Tech.*, Oct. 1938); will appear in Trans. (1939) **135**.

The orientation that appears with low intensity in each of the authors' pole figures of deformed single crystals, which is related to the predominant orientation by a rotation of 180° about the flow direction, is of fundamental importance in the mechanism of cold-rolling of alpha brass, I believe. Crystalline fragments of this orientation would etch differently from the main portion of the deformed crystal and would appear under the microscope as patches or bands. Since the single crystals seem to behave like the individual grains in an aggregate, there would also be areas of differing orientation within a single grain of an aggregate. From this it can be concluded that the phenomenon of duplex orientation in the authors' pole figures is analogous and probably identical with that of etch bands, or deformation bands, in rolled alpha brass. Mathewson and Phillips[23] noticed these bands in 1916, and many investigators have discussed them; I have included a review of the subject in the paper on the structure of iron (ref. 22).

The relation in orientation between major and minor constituents in the pole figures is the twinning relation, or closely approximates this, as one would expect from the work of Samans[24] on the deformation markings in 70:30 brass. I do not think, however, that mechanical twinning is the basis for this relationship, for the gradual increase in visibility of the bands with increasing deformation, noted by Mathewson and Phillips (ref. 23) indicates a progressive rotation of the lattice in adjacent bands away from each other, and not a sudden twinning into the final orientations. The development of deformation bands during compression of iron is definitely a gradual process (ref. 22), unlike twinning.

It seems safe to conclude that the duplex deformation texture of rolled brass is developed from deformation bands much as the double fiber texture of iron is developed during compression. Individual crystals of certain special orientations go homogeneously to a single final orientation, while others, starting from a different orientation, divide into bands and rotate toward different final positions. The relative amounts of material in the two final orientations of a deformed crystal must be a function of the initial orientation of the crystal, and although the authors find only a small amount of the second orientation there will probably be equal amounts of the two in some crystals.

If deformation bands occur in rolled alpha brass, I think they can be anticipated in all face-centered cubic metals and alloys after rolling, for the deformation textures are much alike. There is, in fact, good evidence for them in published photographs of rolled copper, cupronickel, cupronickel-manganese, and silver.

C. H. Mathewson (written discussion).—Dr. Beck appears to agree with us that the relationship between recrystallization and strain-hardening contains many elements of variability and that recrystallization is essentially dependent upon what may be called a secondary lattice distortion apart from the effects that are inherent in the pure shearing action and are doubtless responsible for the major part of the strain-hardening.

Dr. Smith's discussion of the hardness curves should be considered in the light of the following additional explanation. The relation between Brinell and Rockwell F numbers given by Dr. Pickus in his dissertation is practically linear above approximately 90, a point of coincidence on both scales. In this region a difference of one Rockwell number corresponds to some 4½ Brinell numbers but at about 56 Brinell (=66 Rockwell) the steps have become equal and at about 38 the two scales again

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[23] C. H. Mathewson and A. Phillips: Recrystallization of Cold-worked Alpha Brass on Annealing. *Trans.* A.I.M.E. (1916) **54,** 608.

[24] C. H. Samans: The Deformation Lines in Alpha Brass. *Jnl.* Inst. Metals (1934) **55,** 209.

coincide. Here, a difference of one Rockwell number corresponds to approximately half a Brinell number. The entire curve has no appearance of discontinuity, but when it is used for the substitution of Rockwell numbers on a smooth curve of Brinell hardness vs. annealing temperature, such as the one represented in Fig. 18, a step, or irregularity, occurs, as shown in Fig. 17. This seems to be inherent in the variable relation between Brinell and Rockwell numbers throughout the range of plotting and does not require a displacement of points due to interrupted grain growth, as suggested by Dr. Smith.

The absence of twin orientations in strain-hardened alpha brass presumed by Dr. Barrett seems improbable, as it constitutes a rejection of evidence already available in the other direction. The view that twin nuclei generate spontaneously on

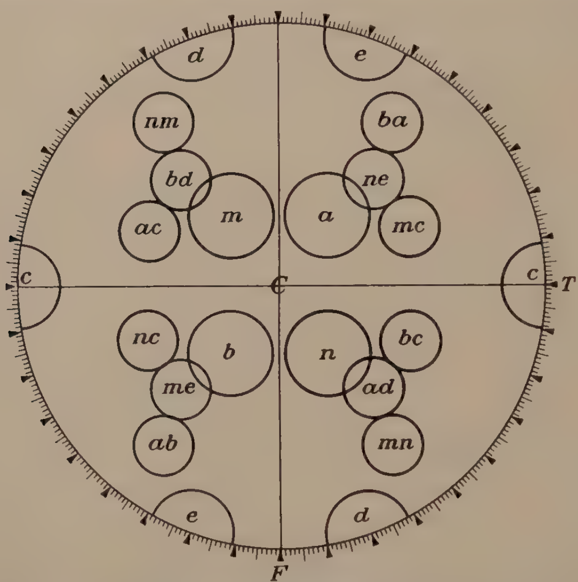

Fig. 20.—New orientations.
a, b, d, c indicate octahedral poles first orientation; m n, e, c, octahedral poles complementary orientation. In twin orientations first letter indicates twinning plane; second letter relocated octahedral pole.

annealing after strain would be more attractive if a prerequisite condition of severe lattice disorganization could be established. In reality abundant twins are seen on annealing after slight deformation (of either single or polycrystalline metal) and it may be imagined that slip is not simple translation in the <110> direction, but a resultant of differentiated movements 30° to the right and left of the slip direction; one producing a twin orientation and the other a return to the original orientation. The process might stop randomly at either end point and thus produce adjacent (thin) lamellae of either orientation.

The first step toward further progress with such an assumption would be to demonstrate the presence of the twin orientations in worked, but unannealed, metal and it is believed that Dr. Samans did this in 1934. The opinion that mechanical twinning, as expressed by a rotation of 180° around F as an axis, is not responsible for the relation between major and minor constituents of the pole figures shown on page 170, is probably correct because this would correspond to twinning by shearing action along the octahedral plane whose pole is at T, and this is not held to be an active plane, at

least in a late stage of the deformation. On the other hand, twinning along the octahedral plane of high resolved shear stress whose pole is shown prominently in the neighborhood of 35° from the center of the projection, Fig. 10, would give a rather interesting new octahedral pole, *ad*, shown in Fig. 20. This seems to offer a better rationalization of the diamond-shaped coverage in the lower right-hand quadrant of Fig. 10 than an assumption of band rotation into a position symmetrical with the major orientation. The entire set of new orientations obtained by twinning along the active slip planes *a* and *b* and the planes *m* and *n* of a possible complementary band are shown in Fig. 20. This may be of value in the interpretation of the pole figure in Fig. 13, from von Göler and Sachs, which according to this view contains poles in the major positions developed from different crystal orientations with or without band formation and secondary poles developed by twinning as an accompaniment of slip on the active planes. Obviously, the complicated mechanism of slip, twinning and rotation must be studied in much greater detail before the exact origin of these textures can be specified. For example, the absence or weak manifestation of minor constituents in Fig. 9 gives poor support to the theory of mechanical twinning, but it may be due to a weakening of intensity maxima from distortion by conjugate slip across the twin lamellae.

Rates of Diffusion of Copper and Zinc in Alpha Brass

By Ernest Kirkendall,* Junior Member A.I.M.E., Lars Thomassen,† and Clair Upthegrove,‡ Member A.I.M.E.

(Detroit Meeting, October, 1938)

The amount of research done in the last few years on the subject of diffusion in solid metals is significant of the importance of this problem. To review the literature dealing with diffusion is unnecessary here. Desch[1] in 1912 reviewed the work that had been done on diffusion in solids and gave a bibliography of the literature published before that time. Mehl's paper in 1936[2] is an excellent review of diffusion in metals and contains a large bibliography. Of importance also for its review and bibliography is an article by A. I. Krynitsky.[3]

While considerable material has appeared in the literature on diffusion in brass, the amount of information is not great compared to that pertaining to some of the other alloys. Most of the information published is of a qualitative nature; that which is quantitative varies considerably. Thus the quantitative determination of the rates of diffusion of copper and zinc in alpha brass by a new method appeared worth while.

In the present investigation the rate of diffusion of zinc in approximately the same composition alpha brass has been determined at three temperatures.

Procedure

The method used consisted of plating copper on a beta brass, heating it to allow diffusion to take place, and measuring the concentration of copper by determining the lattice constant of the alloy. This method is unique in that it uses a beta brass of such a composition that at the temperature at which diffusion takes place the beta brass is saturated with copper. Thus, while the beta brass supplies the zinc, no diffusion takes

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* Instructor of Chemical Engineering, Wayne University, Detroit, Mich.

† Associate Professor of Metallurgical Engineering, University of Michigan, Ann Arbor, Mich.

‡ Professor of Metallurgical Engineering, University of Michigan.

[1] References are at the end of the paper.

place in the beta brass. As fast as zinc is taken from the beta brass, the beta brass changes to alpha brass and all of the diffusion takes place in one phase. Table 1 gives the compositions of the various brasses used.

TABLE 1.—*Brass Analyses*

Brass	Per Cent Zinc	Temperature at Which Used, Deg. C.
A	56.41	600
B	57.52	655
C	58.63	720

Ingots of the compositions given were cast, using zinc of 99.99 per cent purity and copper 99.94 per cent. These were then rolled and annealed in several stages to produce a chemically homogeneous strip ⅛ in. thick. These strips were cut into 4-in. lengths, machined and two surfaces polished until parallel to within less than one half of one thousandth of one inch. Copper was electroplated onto these strips to a depth of about 0.010 in. on each surface, and the bars were heated under vacuum at 450° C. for a few hours, to remove any occluded hydrogen.

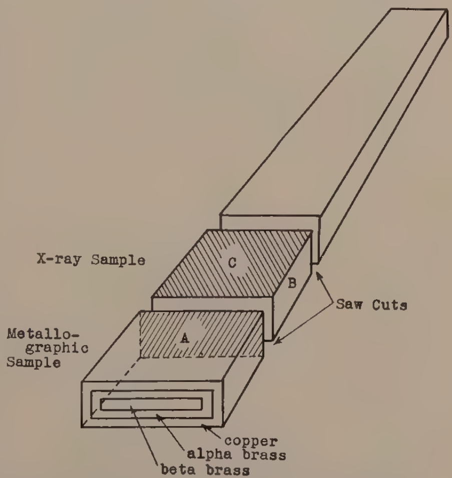

FIG. 1.—SHOWING LOCATION OF SURFACES TO BE EXAMINED ON PLATED BRASS BAR.

Surface *A* is to be exposed when the metallographic sample is mounted in Bakelite. Side *B* and the opposite side are to be ground down to the beta brass before the X-ray sample is mounted in Bakelite with surface *C* exposed.

The degassed copperplated brass bars were now ready for the actual diffusion treatment. A sample ⅜ in. long was cut from one end of each bar, polished, etched and photographed to show the original stock before the diffusion treatment (Fig. 2). The bar was then heated for the prescribed times at the desired temperatures in an electric muffle furnace. The temperatures were controlled to within plus or minus 3° C. At the end of the prescribed time for diffusion, the bar was removed from the furnace and quenched in water. After heating, the flat sides, of which surface *C* (Fig. 1) is a part, were polished to insure their being flat. Two pieces ⅜ in. long were then carefully cut from the bar, and the bar returned to the furnace for further diffusion.

The first sample was mounted in Bakelite with surface *A* (Fig. 1) exposed. This provided a cross section for the photomicrographs.

The second sample was mounted in Bakelite so that surface C was exposed. The second sample was to be used for the X-ray pictures.

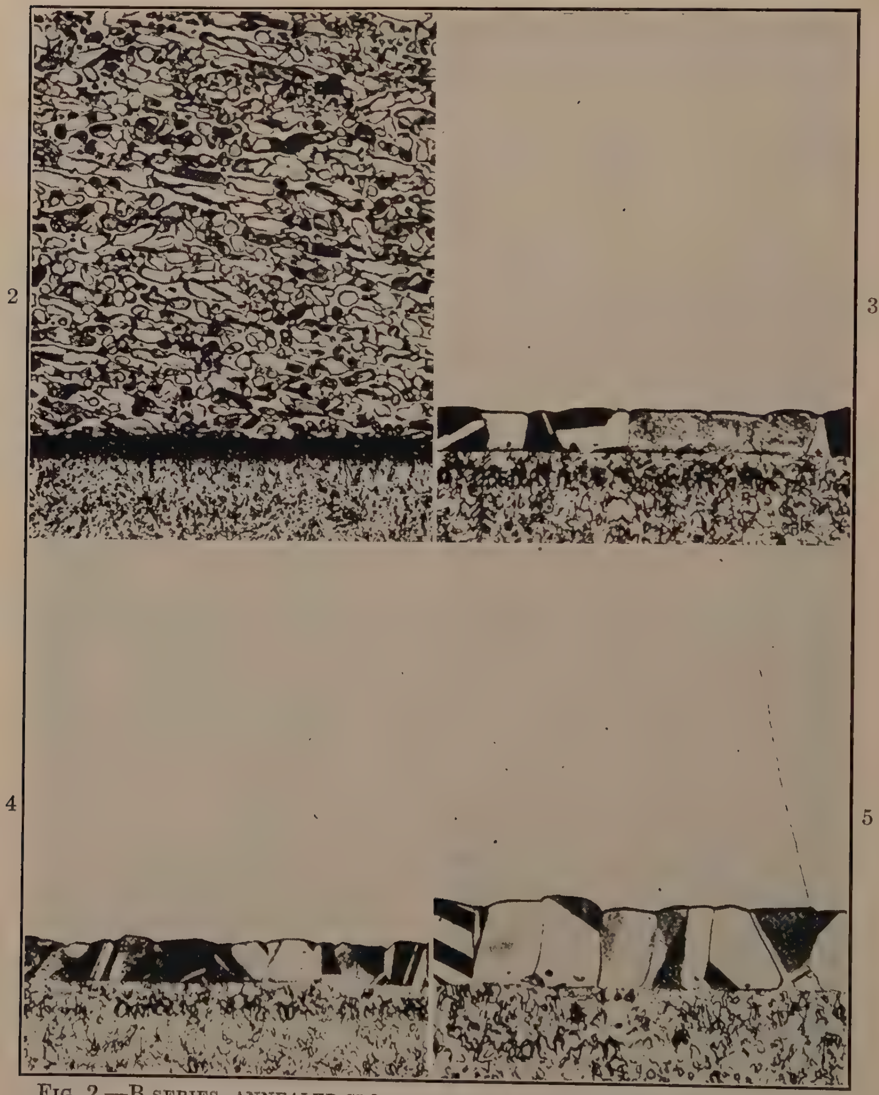

Fig. 2.—B series, annealed stock before diffusion treatment. × 200.
Fig. 3.—B series, heated 1 hour at 655° C. and quenched. × 200.
Fig. 4.—B series, heated 1 hour at 655° C. and quenched. × 200.
Fig. 5.—B series, heated 4 hours at 655° C. and quenched. × 200.

During the heating operation described above, some of the beta brass and some of the copper become alpha brass. This produces a layer of alpha brass, bounded on one side by beta brass and on the other side by pure copper. The alpha brass layer was uniform enough to permit

several X-ray back-reflection pictures to be taken at different depths and thus determine the concentration gradient. The amount of metal diffusing across the original interface was measured by determining the

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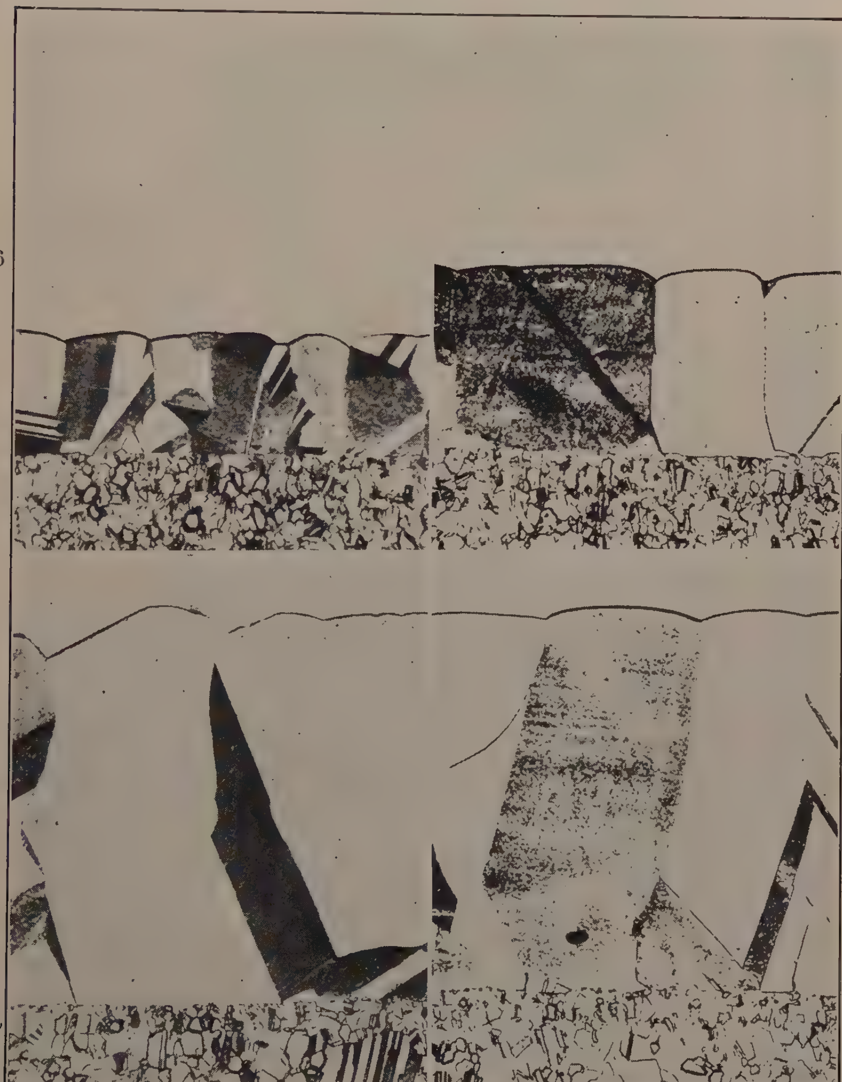

8 9

FIG. 6.—B SERIES, HEATED 10 HOURS AT 655° C. AND QUENCHED. × 200.
FIG. 7.—B SERIES, HEATED 24 HOURS AT 655° C. AND QUENCHED. × 200.
FIG. 8.—B SERIES, HEATED 96 HOURS AT 655° C. AND QUENCHED. × 200.
FIG. 9.—B SERIES, HEATED 96 HOURS AT 655° C. AND QUENCHED. × 200.

depth of the alpha layer metallographically and obtaining from the X-ray data the composition of the alpha phase from the original to the final alpha-beta interface.

Fig. 10. Fig. 11. Fig. 12.

Fig. 10.—A series, heated 24 hours at 600° C. and quenched. × 200.
Fig. 11.—A series, heated 96 hours at 600° C. and quenched. × 200.
Fig. 12.—A series, heated 339 hours at 600° C. and quenched. × 200.

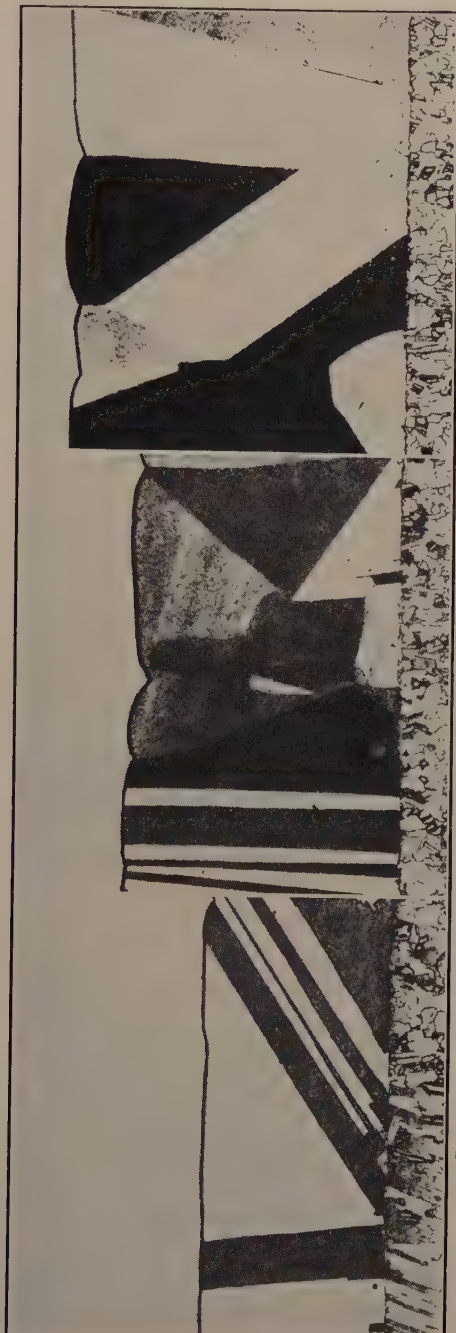

Fig. 13. Fig. 14. Fig. 15.

Fig. 13.—C series, heated 8 hours at 720° C. and quenched. × 200.
Fig. 14.—C series, heated 16 hours at 720° C. and quenched. × 200.
Fig. 15.—C series, heated 24 hours at 720° C. and quenched. × 200.

The X-ray sample was polished to the desired depth, that is about one half of one thousandth of one inch less than the location of the desired back-reflection picture. The remainder of the metal was removed by etching in a 25 per cent aqueous solution of nitric acid. X-ray pictures were taken, each 0.001 to 0.003 in., depending upon the sample. From the location of the lines appearing on the X-ray film, it was possible to calculate the lattice constant for the brass at the depth examined. From the lattice constant it was possible to calculate the composition of the alpha brass at each of the layers examined.

The X-ray tube used was a gas tube with a cobalt target. The sample was placed in the center of the camera and rotated by a small motor in a plane perpendicular to the X-ray beam during the exposure. Carefully reduced gold powder was sprinkled as a thin layer on each sample to act as a reference substance. This made it unnecessary to know accurately the film-to-sample distance and has been shown to give very accurate results.

Results

Figs. 2 through 15 show the photomicrographs of the samples at 200 diameters. The first eight photomicrographs show all of the samples for the B series. The remaining six show the three more important samples of each of the other series. An alpha brass layer is formed on each side of the original interface. The alpha layer inside of the original interface is composed of large columnar grains with a definite final interface caused by the change in phase. The higher copper alpha brass layer outside the

TABLE 2.—*Effect of Time and Temperature on Diffusion*

Sample No.	Temperature, Deg. C.	Time, Hr.	Penetration,[a] In.
A2	600	2	0.0009
A3	600	9	0.0018
A4	600	24	0.0030
A5	600	96	0.0054
A6	600	339	0.0094
B2	655	1	0.0010
B3	655	4	0.0021
B4	655	10	0.0030
B5	655	24	0.0048
B6	655	96	0.0098
C2	720	1	0.0016
C3	720	3	0.0028
C4	720	8	0.0048
C5	720	16	0.0069
C6	720	24	0.0086

[a] Penetration was measured as the distance between the original interface and the final alpha-beta interface.

original interface shows no change in grain shape nor a definite final interface, since copper and alpha brass have the same atomic arrangement. Fig. 2 shows the degassed stock for series B just before the diffusion treatment. This sample after cooling slowly has an alpha plus beta core surrounded by the copperplate. Figs. 3 and 4 as well as 8 and 9 are

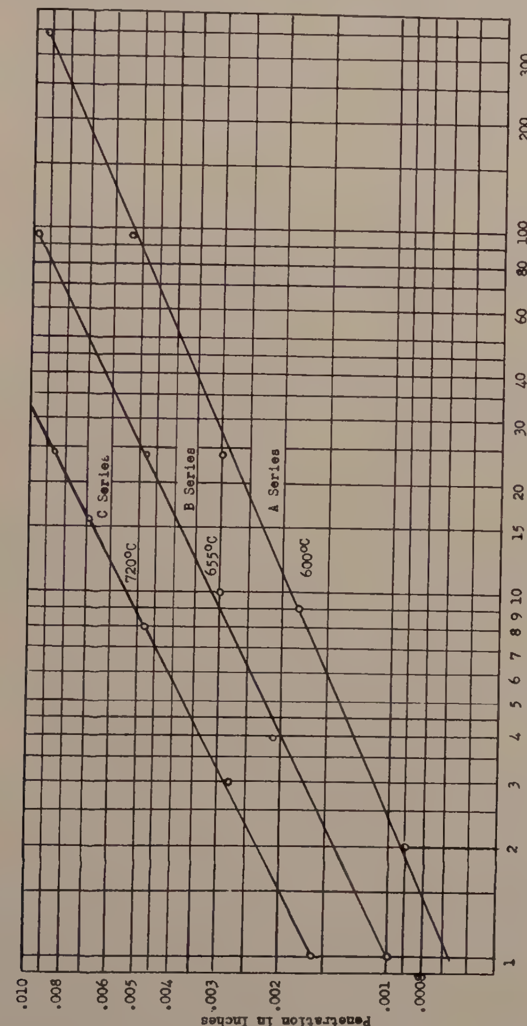

FIG. 16.—EFFECT OF TIME AND TEMPERATURE ON DIFFUSION IN ALPHA BRASS.

duplicates as far as measurements are concerned. Taken at different positions on the same sample, these show that the alpha layer formed between the original and final interface is uniform in depth.

Since the original and final alpha-beta interfaces are definite, all calculations are based on the diffusion of copper into this layer. An equal number of atoms of zinc must diffuse out of this layer to produce a higher

copper alpha layer just outside the original interface, but its outer boundary is not definite microscopically. The side showing the new interface is used because in determining the amount of metal diffusing only the change on one side of the original interface need be known. Table 2 gives the distance between the original and final interfaces for each sample. These data are shown on a log-log plot of time versus temperature in Fig. 16. Three straight lines are produced.

The quantitative treatment of diffusion in solid metals is based on Fick's law:

$$dm = -DA(dc/dx)dt \tag{1}$$

where dm is the amount of matter diffusing in time dt in the direction of a concentration gradient $-dc/dx$ and across an area A. D is the diffusion coefficient. Thus D represents the number of grams of material diffusing across an area of one square centimeter in one second and in the direction of a concentration gradient of one gram per cubic centimeter per centimeter. D is constant only if the temperature and composition remain constant. A change in phase causes D to change abruptly and a change of concentration within a phase produces a corresponding change in D.

In computing rates of diffusion, it is necessary to know the concentration gradient at the point where the diffusion rate is being measured as well as the amount of metal transferred. Both of these factors can be obtained by determining the composition of the brass at various locations by means of X-ray pictures. The results obtained are given in Tables 3, 4 and 5.

Plotting the X-ray data showing the variation in zinc content at various depths, a graph similar to Fig. 17 is obtained. When the distance between the original and final interfaces was divided into 10 equal

TABLE 3.—*X-ray Data for Master Curve for Series A*

Sample No.	Total Penetration, In.	Location of Picture		Lattice Constant, Å.	Per Cent Zinc
		In.	Units		
A5	0.0054	+0.0040	+7.4	3.6116	1
A5	0.0054	0.0000	0.0	3.6818	32
A5	0.0054	−0.0020	−3.7	3.6905	35.5
A5	0.0054	−0.0040	−7.4	3.6940	37
A6	0.0094	+0.0075	+8.0	3.6098	0
A6	0.0094	+0.0055	+5.9	3.6144	2
A6	0.0094	+0.0025	+2.7	3.6651	25
A6	0.0094	0.0000	0.0	3.6802	31.5
A6	0.0094	−0.0030	−3.2	3.6878	34.5
A6	0.0094	−0.0065	−6.9	3.6946	37

TABLE 4.—*X-ray Data for Master Curve for Series B*

Sample No.	Total Penetration, In.	Location of Picture		Lattice Constant, Å.	Per Cent Zinc
		In.	Units		
B5	0.0048	+0.0040	+8.3	3.6147	2.5
B5	0.0048	+0.0028	+5.8	3.6201	5
B5	0.0048	+0.0008	+1.7	3.6612	23.5
B5	0.0048	−0.0004	−0.8	3.6799	32
B5	0.0048	−0.0020	−4.2	3.6850	33
B6	0.0098	+0.0083	+8.5	3.6096	0
B6	0.0098	+0.0060	+6.1	3.6192	4.5
B6	0.0098	+0.0051	+5.2	3.6364	13
B6	0.0098	+0.0041	+4.2	3.6492	18.5
B6	0.0098	+0.0025	+2.5	3.6585	22.5
B6	0.0098	0.0000	0.0	3.6742	29
B6	0.0098	−0.0020	−2.0	3.6808	31.5
B6	0.0098	−0.0038	−3.9	3.6874	34
B6	0.0098	−0.0057	−5.8	3.6893	35
B6	0.0098	−0.0082	−8.4	3.6934	36.5

TABLE 5.—*X-ray Data for Master Curve for Series C*

Sample No.	Total Penetration, In.	Location of Picture		Lattice Constant, Å.	Per Cent Zinc
		In.	Units		
C4	0.0048	+0.0045	+8.7	3.6111	0
C4	0.0048	+0.0020	+4.2	3.6558	21
C4	0.0048	0.0000	0.0	3.6786	31
C4	0.0048	−0.0020	−4.2	3.6870	34
C4	0.0048	−0.0035	−7.3	3.6897	35
C5	0.0069	+0.0055	+8.0	3.6122	1
C5	0.0069	+0.0035	+5.1	3.6370	13
C5	0.0069	+0.0010	+1.4	3.6600	23
C5	0.0069	−0.0005	−0.7	3.6759	29.5
C5	0.0069	−0.0030	−4.3	3.6844	33
C5	0.0069	−0.0055	−8.0	3.6889	35
C6	0.0086	+0.0060	+7.0	3.6170	3.5
C6	0.0086	+0.0035	+4.1	3.6449	17
C6	0.0086	+0.0015	+1.7	3.6630	24.5
C6	0.0086	−0.0005	−0.6	3.6751	29
C6	0.0086	−0.0025	−2.9	3.6829	32.5
C6	0.0086	−0.0045	−5.2	3.6876	34.5
C6	0.0086	−0.0070	−8.1	3.6897	35

units and the zinc content at the beginning of each unit was measured and replotted using units as abscissas, the curves for various times at any one temperature coincided. The curve resulting from this procedure is designated as the master curve in this paper. It was not possible to obtain enough X-ray data to determine the shape of the individual curves unless diffusion had continued long enough to produce a diffusion band at least 0.005 in. thick. Since this minimum diffusion band was not obtained for all samples, a master curve having units for abscissas was obtained as described above, using X-ray data for the samples having a distance

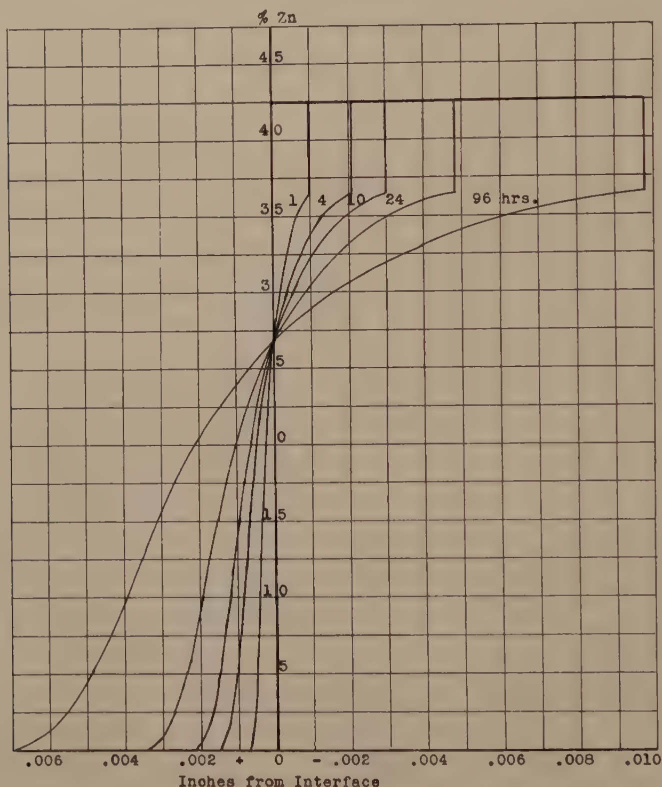

FIG. 17.—DIFFUSION CURVES FOR SERIES B. EFFECT OF TIME ON DIFFUSION AT 655° C.

between initial and final alpha-beta interfaces of 0.005 in. or more. Fig. 17, showing complete diffusion curves for samples having diffusion bands less than 0.005 in., was obtained from the master curve as described later.

Fig. 18 shows the master curve for the B series. Actually, to plot a point on this graph according to the method outlined above, the abscissa in units was obtained by measuring the distance of the surface used for the X-ray picture from the initial copper-brass interface, dividing this distance by the distance between the initial and final alpha-beta interfaces

for that sample (as obtained metallographically) and multiplying by 10. Since the X-rays penetrate to a considerable depth, the compositions as determined from the lattice constants were plotted as horizontal lines 0.001 in. long. The left-hand end of these lines gives the abscissas corresponding to the location of the surface for the X-ray picture. The following conditions were satisfied in drawing the master curves:

1. The areas on both sides of the interface were equal; i.e., an equal number of zinc and copper atoms exchanged places.

2. Both master curve and its first derivative were smooth.

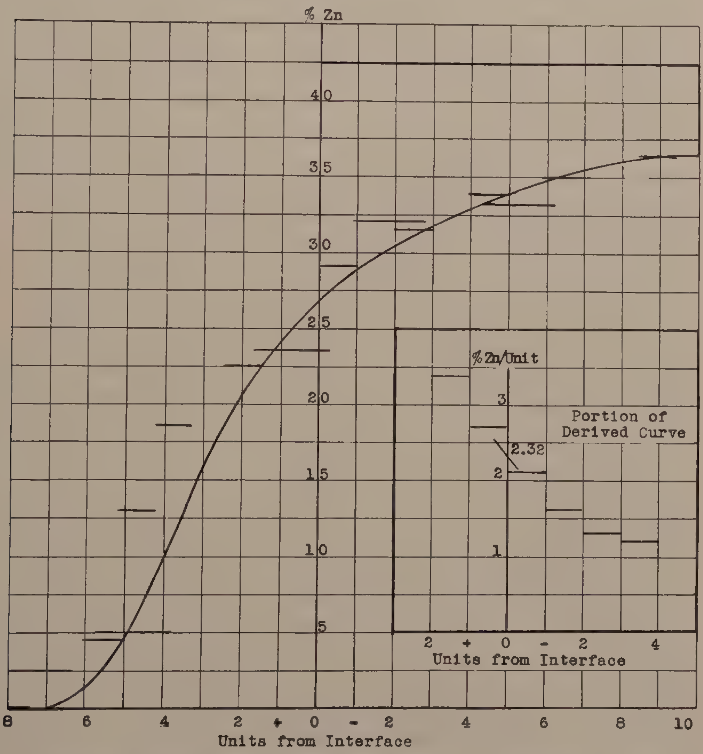

FIG. 18.—MASTER CURVE FOR SERIES B. SHAPE OF DIFFUSION CURVE AT 655°.

The master curves for all three of the series are shown together in Fig. 19.

The slopes of the master curves were obtained at the initial interface by plotting the derived curve in the vicinity of the interface (Fig. 18). This slope gave the concentration gradient when the units were changed to the corresponding number of inches for each sample. The factor for this conversion was 10 times the reciprocal of the distance from the initial to the final alpha-beta interface.

Fig. 17 was obtained by taking points from the master curve for series B and multiplying the abscissa by a factor. This factor was $\frac{1}{10}$ of the distance from the initial to the final alpha-beta interface. The amount of zinc, m, diffusing out of the beta brass may be found graphically from such curves as are found in Fig. 17. A square unit as obtained by this graphic integration and used later in the calculations is 2.5 per cent of the metal in a plate 1 sq. cm. in area and 0.001 in. thick.

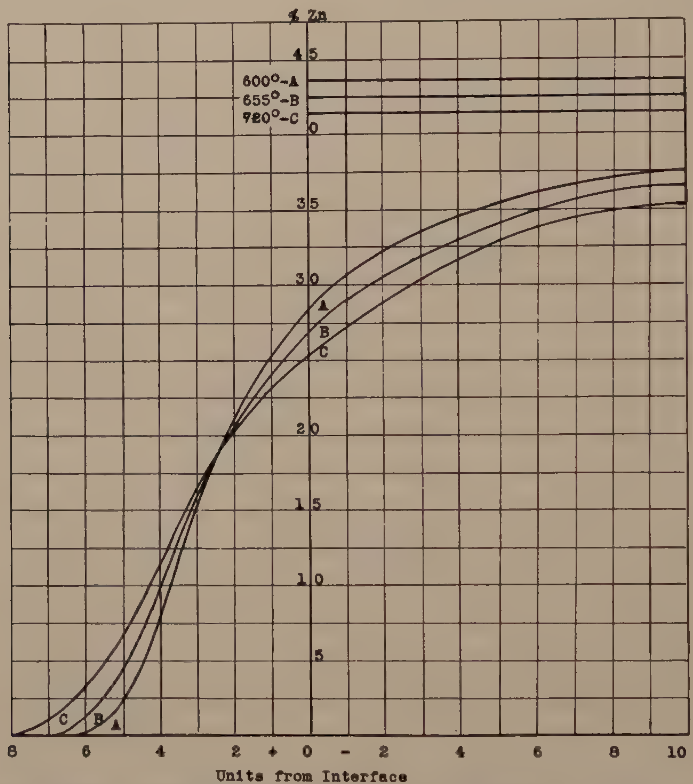

FIG. 19.—MASTER CURVES FOR SERIES A, B AND C. EFFECT OF TEMPERATURE ON SHAPE OF DIFFUSION CURVES.

The calculation of the diffusion coefficient was accomplished as follows: Rewriting Fick's law, and using unit area and small increments instead of differentials gives:

$$D = -\Delta m/(\text{mean } dc/dx)\Delta t \qquad [2]$$

A simplified integration was carried out using five increments, with dc/dx known at the beginning of each increment. However, since a plot of m versus dc/dx was not linear, it would not be desirable to use an arithmetic mean. The mean dc/dx used was chosen so that in each

increment the same amount of metal diffused with a concentration gradient dc/dx greater than that chosen, as diffused with a concentration gradient dc/dx less than the mean chosen. The values for each of the

TABLE 6.—*Calculation of D for Series A*

	2 Hr.	9 Hr.	24 Hr.	96 Hr.	339 Hr.
m square units	3.24	6.48	10.80	19.4	33.8
dc/dx, per cent per 0.001 in.	29.65	14.83	8.90	4.94	2.84

Δm square units	3.24	4.32	8.6	14.4
Mean dc/dx, per cent per 0.001 in.	19.70	11.05	6.35	3.63
Δt hr	7	15	72	243
$D(10^{-11})$, sq. cm. per sec.	10.5	11.7	8.5	7.3

TABLE 7.—*Calculation of D for Series B*

	1 Hr.	4 Hr.	10 Hr.	24 Hr.	96 Hr.
m square units	3.70	7.77	11.10	17.70	36.3
dc/dx, per cent per 0.001 in.	23.20	11.04	7.73	4.83	2.37

Δm square units	4.07	3.33	6.66	18.54
Mean dc/dx, per cent per 0.001 in.	15.0	8.95	5.95	3.25
Δt hr	3	6	14	72
$D(10^{-10})$, sq. cm. per sec.	4.1	2.4	3.6	3.6

TABLE 8.—*Calculation of D for Series C*

	1 Hr.	3 Hr.	8 Hr.	16 Hr.	24 Hr.
m square units	6.08	10.64	18.24	26.22	32.67
dc/dx, per cent per 0.001 in.	12.50	7.14	4.17	2.90	2.32

Δm square units	4.56	7.60	7.98	6.45
Mean dc/dx, per cent per 0.001 in.	9.05	5.26	3.38	2.51
Δt hr	2	5	8	8
$D(10^{-9})$, sq. cm. per sec.	1.14	1.30	1.32	1.45

quantities used in equation 2 as well as the calculated D's for series A, B and C, are given in Tables 6, 7 and 8.

The four D's for each temperature as obtained by equation 2 were then weighted according to the amount of metal diffused during the time that each was measured and averaged. These values are given in Table 9.

TABLE 9.—*Diffusion Coefficients for Various Temperatures*

Series	Temperature, Deg. C.	Diffusion Coefficient, Sq. Cm. per Sec.
A	600	8.6×10^{-11}
B	655	3.5×10^{-10}
C	720	1.3×10^{-9}

DISCUSSION OF RESULTS

Of the various equations used to calculate diffusion coefficients at different temperatures, the equation

$$D = Ae^{-Q/RT} \qquad [3]$$

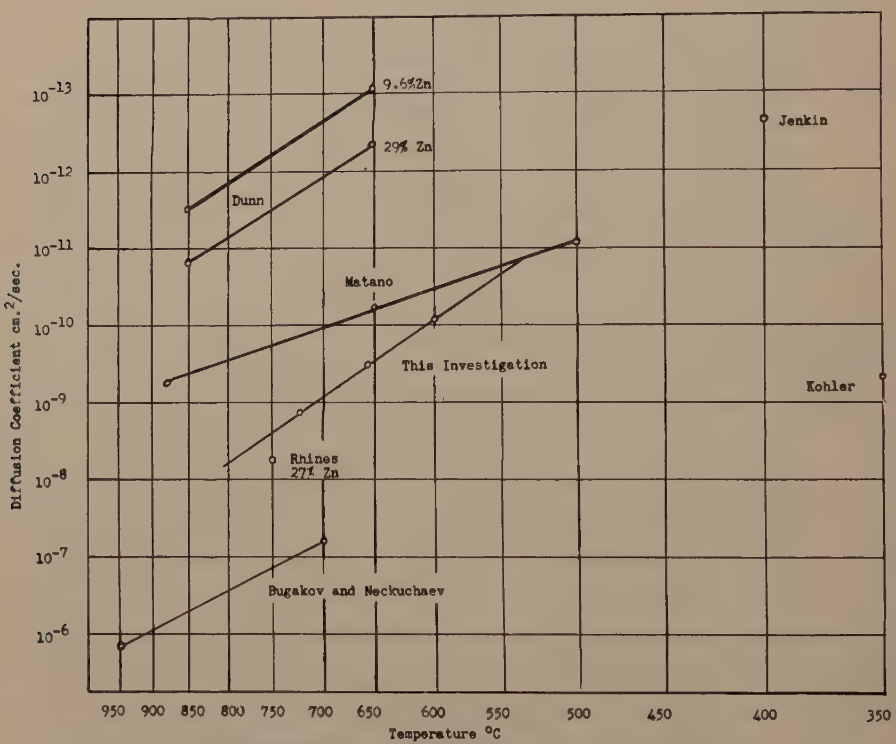

FIG. 20.—DIFFUSION COEFFICIENTS FOR ZINC IN ALPHA BRASS.

is probably the most commonly used. D is the diffusion coefficient, A is a constant, e is the base of the natural logarithms, Q is the heat of diffusion per gram atom, R is the gas constant and T is the absolute temperature. By expressing this equation in the form

$$\log D = \log A - (Q/RT) \log e \qquad [4]$$

Q may easily be determined algebraically if the value of D is known at

each of two temperatures, or Q may be determined graphically by plotting the logarithm of D against $1/T$ and finding the slope of the resulting straight line. Q really expresses the effect of temperature on the rate of diffusion, and often is given along with the diffusion coefficients.

Fig. 20 is a plot of log D versus $1/T$. The various published values of D are shown on this plot as well as the results of this investigation. The wide variation in results is apparent. In most cases, sufficient information concerning the experimental procedure has not been published to make it possible to make a definite comment on the reason for these discrepancies. While one would not expect the data to fall on a single diagonal straight line, inasmuch as D varies considerably with the concentration of the alpha brasses used, the wide discrepancy is probably due not so much to the different brasses used as it is to the assumption made by some investigators in order to facilitate their calculations that D does not vary with concentration. In the author's work, Fick's fundamental diffusion law was used. Calculations were based on the composition of the brass at the original interface, which was constant.

Using equation 3 and the data in Table 9, Q may be calculated and is found to be 39,100 cal. per gram atom.

This value for Q, which can also be obtained from the slope of the lines in Fig. 20, is very close to that of Dunn's work as well as Bugakov and Neskuchaev's work. In other words, while the diffusion coefficients are different, they show the same variation with temperature. Rhines' work[4,5] gives a value for the diffusion coefficient very close to that of the authors' (Fig. 20).*

The complete Dushman-Langmuir equation:

$$D = (Q/Nh)\delta^2 e^{-Q/RT} \qquad [5]$$

requires only one value of D for its solution. N is the Avogadro number, h is Planck's constant and delta is the interatomic distance. Although several experimenters have doubted its veracity, it is possible that lack of accurate measurements may account for this skepticism. Using the data of Table 9 and a delta of 2.61×10^{-8} cm., Q will be found to have the following values:

$Q = 38{,}000$ cal. per gram atom at 600° C.; 37,700 at 655° C., and 37,800 at 720° C.

The agreement between the value for Q as obtained by the Dushman-Langmuir equation (about 38,000 cal. per gram atom) and the more generally accepted equation 3 (about 39,000 cal. per gram atom) is very good.

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* Rhines' work was published in part in 1937 and later in full subsequent to the completion of the present work.

Summary

The purpose of this investigation was to determine the rate of diffusion of zinc and copper in alpha brass, and to ascertain the effect of temperature on the rate of diffusion.

Three diffusion coefficients have been determined at three different temperatures on substantially the same alpha brass. From these results it is possible to calculate the probable rate of diffusion in this alpha brass at any temperature below its melting point, by means of either of two equations cited in this paper.

The method used has made it possible to eliminate any uncertainties concerning the variation of rates of diffusion with concentration as well as those concerning the superficial area of a porous surface, factors that have entered into earlier investigations.

The coefficients of diffusion as determined in this investigation are given in Table 10. These rates of diffusion have been shown to fit the

Table 10.—*Coefficients Determined in This Investigation*

Diffusion Coefficient, Sq. Cm. per Sec.	Temperature, Deg. C.	Composition of Brass, Weight Per Cent Zinc
8.6×10^{-11}	600	28.3
3.54×10^{-10}	655	26.8
1.31×10^{-9}	720	25.3

generally accepted equation

$$D = Ae^{-Q/RT}$$

which shows the effect of temperature on diffusion. The value of Q in this equation has been found to be 39,000 cal. per gram atom, from the results listed.

The substitution of any one of the diffusion coefficients from Table 10 in the less empirical equation

$$D = (Q/Nh)\delta^2 e^{-Q/RT}$$

gives a value for Q of about 38,000 cal. per gram atom, which is in exceptional agreement with the value of Q just mentioned.

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DISCUSSION

(Robert F. Mehl presiding)

F. K. Savage,* Elkhart, Ind. (written discussion).—In electrodepositing any metal upon another, the matter of films must be carefully considered. It is possible under carefully controlled conditions to electrodeposit one metal upon another and maintain the same crystal orientation in the deposit as that of the basis metal. At times the grains in the deposit are a continuation of the grains in the surface of the basis metal. Films of practically any nature on the basis metal inhibit this grain continuation and the structure of the deposit has no relation to it. These films may be of an alkaline nature like those obtained from an alkaline cleanser, oxides of various types resulting from overcleaning or exposure to air, or a smut of other metals picked up some place in the cleaning operation. It seems logical to believe that there might be inconsistent results in the rates of diffusion if it took place through a film of some nature in one case and through a perfect film-free metal to metal bond in another. The fact that the deposit is adherent is no proof of a perfect bond or the absence of films in the interphase.

The authors stated that the beta brass basis metal was rolled and annealed several times to produce a perfectly homogeneous strip. Although the electrodeposit was pure copper, the conditions of plating, temperature, current density, agitation and bath composition may affect the grain size and conformation tremendously. This, added to the fact that the grains of an electrodeposit tend to orient themselves always normal to the surface in long needlelike crystals, might give rise to considerable variation between different samples. This variation, if it is a factor in the rate of diffusion, might lead to erratic results, particularly in view of the fact that the deposit was not rolled and annealed as was the basis metal.

E. O. Kirkendall, L. Thomassen and C. Upthegrove (written discussion).—The method used by the authors to avoid a film at the interface consisted of machining the brass strips, polishing them by hand with emery paper, immediately cleaning the strips with benzene to remove any oil films or abrasive, and then electroplating. It is not contended, however, that the crystal orientation of adjacent crystals in plate and base metal are the same, since beta brass is body-centered cubic and copper is face-centered cubic.

While the conditions for electroplating were all substantially the same, slight variations in grain size and shape might arise. The effect of such variations was avoided, since rates of diffusion were measured over increments of time and the first increment of time of one or two hours was not used in making calculations. Thus recrystallization of the plate had an opportunity to take place before affecting the measured diffusion rate. The grain size would be characteristic of the temperature at which diffusion took place, as would be true for most commercial diffusion problems.

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* Electrochemical Engineer, C. G. Conn, Ltd.

The Martensite Transformation in Beta Copper-aluminum Alloys

By Alden B. Greninger,* Junior Member A.I.M.E.

(New York Meeting, February, 1939)

That metallographic structures analogous to the martensite of steel may be found in certain copper-aluminum and copper-tin alloys has been known for many years; similar structures recently were found in certain copper-zinc alloys.[1] In all three of these alloy systems the martensite structures result from transformation of the metastable β phase when the speed of cooling from the β range is sufficiently high to suppress decomposition into equilibrium phases.†

In the normal decomposition of solid solutions into equilibrium phases, diffusion is needed to bring about the necessary changes in concentration, and the rate of reaction falls almost to zero at temperatures slightly above room temperature. The rates of reaction for martensite processes, however, are not dependent upon temperature; the transformation does not require readjustments of concentration. For example, the martensite transformation in 60:40 (β) copper-zinc does not begin until the temperature has dropped to about minus 30° C., and then continues down to minus 130° C. and probably even at lower temperatures.[1] Furthermore, martensite processes apparently proceed only while the temperature is falling, within the proper range, and cease completely while the temperature is held constant;‡ and they cannot be suppressed by extremely rapid cooling although the rate of cooling for some alloys may be increased to over 10,000 times the critical cooling velocity.

Isaitschew, Kaminsky and Kurdjumow[2] account for these observed behaviors of martensite processes by postulating that the mechanism: " . . . consists in a regular rearrangement of the lattice in such a way

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* Assistant Professor of Metallurgy, Graduate School of Engineering, Harvard University, Cambridge, Mass.

[1] References are at the end of the paper.

† The minimum cooling speed that will accomplish this end is usually referred to as the critical cooling velocity.

‡ Although experimental data accumulated by many investigators during the past 10 or 15 years are almost conclusive in establishing this as a fact, the point has been given little attention by many metallurgists. The martensite-time relationship will be discussed at length in a future publication dealing with the martensite transformation in iron-carbon alloys.

that the relative displacement of neighboring atoms does not exceed the interatomic distances and the atoms do not interchange places." This statement fortunately avoids the use of the term "shearing process," so often applied to martensite transformations, and focuses attention on the more general picture of "regular lattice rearrangement without concentration changes." Patently, there is need for a considerable amount of crystallographic data in order that the martensite mechanism may be described more precisely. Recent studies of orientation habits of martensite plates in copper-zinc,[1] copper-tin,[1] and hypereutectoid iron-carbon alloys[3] have shown that these plates, although possessing excellent parallelism, do not form along any principal crystallographic

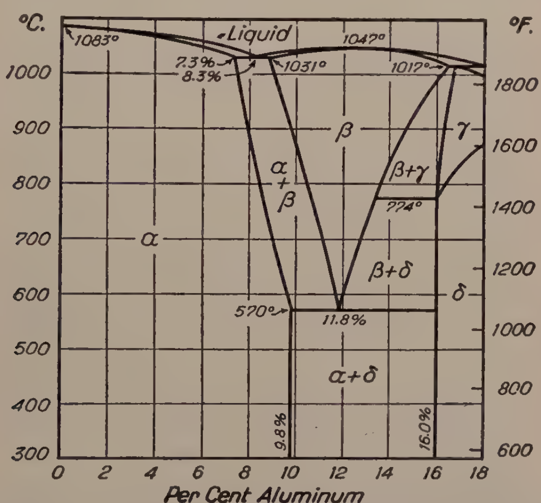

FIG. 1.—COPPER-RICH PORTION OF THE COPPER-ALUMINUM EQUILIBRIUM DIAGRAM. (From *National Metals Handbook.*)

planes of the matrix lattice;* i.e., their orientation habits are irrational. It appears desirable to extend these data to include the martensite structures in β copper-aluminum alloys; in these the relatively large size of the martensite plates should permit a determination of both orientation habit and lattice relationships for an individual martensite plate.

PREVIOUS WORK

The copper-rich portion of the copper-aluminum equilibrium diagram is shown in Fig. 1. The crystal structures of the equilibrium phases found in this section of the diagram are as follows: alpha, face-centered

* The results of Greninger and Troiano on the orientation habit of martensite in hypereutectoid steel have recently been confirmed by Phragmen.[4]

cubic;[5,6] beta, body-centered cubic, random;[7] delta, γ brass structure, ordered;[5] gamma, uncertain.*

The eutectoid $\alpha + \delta$ has a metallographic structure closely resembling that of pearlite[8] in steel and is obtained only with very slow furnace cooling (about 1° C. per minute). If the velocity of cooling from the β range is of the order of 1° per second† (for compositions near the eutectoid), the formation of eutectoid is suppressed and the structure at room temperature is the so-called acicular β, or β' martensite. A most elucidative study of the transformations in β copper-aluminum has been made by Wassermann,[7] using a high-temperature X-ray camera with single-crystal specimens of composition 11.9 and 12.7 per cent Al. X-ray patterns obtained from specimens containing 12.7 per cent Al at temperatures between 580° and 750° C. showed only lines of a disordered body-centered cubic lattice; while patterns taken at 320° C., after rapid cooling from 630° C., showed lines of an ordered body-centered cubic lattice (which Wassermann has named β_1). At room temperature the specimens consisted entirely of β'. Additional X-ray work showed that the β' structure remains unchanged on tempering up to 300° C. (exposure times varied between 2½ and 3 hr.); at 310° C. both β' and β_1 were present, while at 320° C. the specimen again consists entirely of β_1. At 350° C. lines of α and δ appeared during the 3-hr. exposure. Thus, upon "rapid" cooling from the β range, the transformations are $\beta \rightarrow \beta_1 \rightarrow \beta'$, and upon reheating, $\beta' \rightarrow \beta_1 \rightarrow \alpha + \delta \rightarrow \beta$; the transformation $\beta_1 \rightleftarrows \beta'$ is completely reversible. Wassermann made no attempt to measure the temperature of ordering on cooling; he places the transformation range of $\beta_1 \rightarrow \beta'$ for 12.7 per cent Al at 280° to 300° C.

Wassermann's results have been confirmed and extended by Kurdjumow and co-workers[2,9–12,19,20] with thermal, X-ray, and microscopic methods. Thermal analyses on an alloy of 12 per cent Al showed two sharp heat effects (at 500° and 380° C.) on cooling, and a weak effect (at 450° C.) and a sharp effect (at 525° C.) on heating;[11] apparently changes in cooling velocity had no effect on the temperatures of the two cooling points. The upper point was ascribed to the transformation $\beta \rightleftarrows \beta_1$ and the lower point to $\beta_1 \rightleftarrows \beta'$. Working with alloys of higher aluminum content, Kurdjumow and Stelletzky[10] discovered a new martensite lattice having a crystal structure different from that of β', which they

* Bradley and Jones[5] state that a sample of 15.9 per cent Al quenched from 1000° C. gave an X-ray pattern identical to that of the same alloy annealed at 500° C.; they conclude that γ phase must be the same as δ. No high-temperature X-ray work has been done in the γ field.

† There has been no systematic work on critical cooling velocities for β copper-aluminum alloys. The cooling speeds and resulting structures referred to here are given by Wassermann[7] for a specimen containing 12.7 per cent Al. It is known that the critical cooling velocities are considerably higher for compositions that depart substantially from the eutectoid.

named γ'. Gawranek, Kaminsky and Kurdjumow[9] extended this work and determined, by means of cooling curves, martensite transformation temperatures for $\beta_1 \rightarrow \gamma'$ for alloys of compositions between 12.9 and 13.5 per cent Al. Specimens (size not stated) were first quenched from the β range into an oil bath at 250° to 300° C. and thermal curves were then recorded with the specimens cooling in air at a rate of about 5° C. per second. End structures were determined by X-ray methods. For each alloy, only one heat effect was observed between 300° C. and room temperature; and the temperature-versus-composition curve for $\beta_1 \rightarrow \gamma'$ was found to be continuous with that for $\beta_1 \rightarrow \beta'$. A summary of their results is shown graphically in Fig. 2. The curve here represented is a counterpart of the familiar Ar'' curve for iron-carbon alloys. According

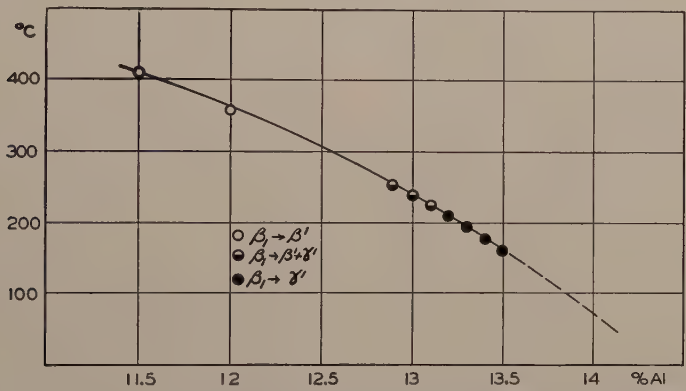

FIG. 2.—INFLUENCE OF COMPOSITION ON MARTENSITE TRANSFORMATION TEMPERATURE IN β COPPER-ALUMINUM ALLOYS.
From the work of Gawranek, Kaminsky and Kurdjumow.[9]

to these authors, β' results from rapid cooling of alloys containing less than 12.9 per cent Al; a mixture of β' and γ'* from alloys between 12.9 and 13.1 per cent Al and γ' only from alloys above 13.1 per cent Al. Thermal curves obtained by reheating γ' to 400° C. showed no discontinuities; the writers conclude that the transformation $\beta_1 \rightarrow \gamma'$ is irreversible. An X-ray pattern from an alloy of 14.7 per cent Al quenched from the β range to room temperature contained only lines of β_1 (body-centered cubic plus superlattice lines). Thus the ordering process in this alloy cannot be suppressed by quenching, and the martensite transformation temperature, as would be expected from an extrapolation of the curve of Fig. 2, is below room temperature. Microscopic work by Gridnew and Kurdjumow[12] showed the metallographic structure of β' to be almost identical with γ'; the only difference noted was that γ' "needles" often contained apparent twin bands.

* Gawranek and co-workers state that this "two-phase region" is probably due to variations in composition within the specimens.

Obinata and Hayashi[13] have recently restudied the transformations in the eutectoid alloy by means of X-ray, electric resistance, and microscopic methods. Specimens containing 12.66 per cent Al were heated and cooled in an evacuated high-temperature microscope stage and a cinematographic record obtained of the changes in microstructure due to the $\beta_1 \rightleftarrows \beta'$ transformation. They observed that, for this alloy, the acicular structure of β' begins to form at about 300° C. on cooling and disappears gradually at about 410° C. on heating. Similar microscopic work performed by Gridnew (ref. 2, p. 366) showed that a single β' martensite plate forms in less than one-tenth of a second. Isaitschew, Kaminsky, and Kurdjumow[2] recently announced that the crystal structures of both β' and γ' have been determined in their laboratory. They describe γ' as hexagonal close-packed with an ordered arrangement of atoms; β' differs from the γ' in that the [00.1] direction is at an angle of 2° to the (00.1) plane normal, and the angle between the planes (10.0) and (01.0) differs about 1° from 120°. These writers also remark upon the fact that β' can be transformed into γ' by mechanical deformation; they state: "After deformation, some lines on the Debye patterns of the β' phase merge together, giving broad lines; the new line system becomes analogic to the line system of the γ' phase."

Smith and Lindlief[8] studied microscopically the decomposition of β at constant temperatures below the eutectoid; they discovered that subcritical transformation of the eutectoid alloy produced a microconstituent consisting of "rosette-shaped particles." The lattice structure of this constituent, and its relation to the other five lattices in this region of the diagram, remains unknown.

Heat-treatment and Microstructures

The alloys used in this study were prepared from copper* of extreme purity (redeposited series-refined cathodes), and high-purity aluminum* containing the following impurities: Si, 0.005 per cent; Fe, 0.003 and Cu, 0.004 per cent. The copper and aluminum were melted in Acheson graphite crucibles in a nitrogen atmosphere, stirred with a graphite rod, and allowed to solidify in the furnace to produce a large β grain size. In all ingots the β grain size was greater than ¼ in.; often single β crystals were produced. Ingot size was ½ in. dia. by 1½ in. long. Specimens cut from these ingots were first heated for about 18 hr. at 1000° C. to promote homogeneity. Some specimens used in the orientation work received a homogenizing treatment of only 1 hr. at 1000° C. Chemical analyses performed on the solution-annealed specimens were as follows: alloy No. 1, 9.29 weight per cent Al; No. 2, 12.45; No. 3, 13.22; No. 4, 13.60; No. 5, 14.74; No. 6, 15.35.

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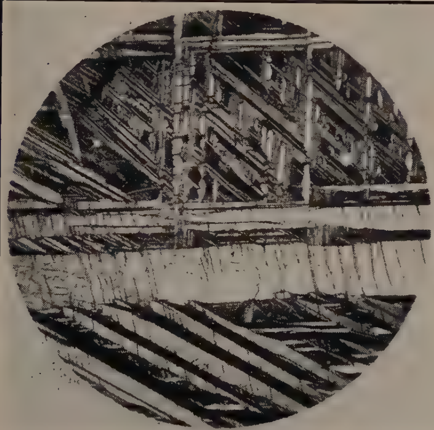
* The copper was kindly supplied by Mr. S. Skowronski, of the Raritan Copper Works; the aluminum, by Mr. G. F. Sager, of the Aluminum Company of America.

Specimens of two different sizes were used in these preliminary heat-treatment studies. Those used for detailed examinations of microstructure were ½ in. dia. by ⅜ in. and those used for rotating-crystal X-ray patterns were about 1/32 by 1/32 by ¼ in. in size. The latter will be referred to hereinafter as "slivers." Polished surfaces of both β' and γ' were found to be highly anisotropic in reflected plane-polarized light, and for these structures examinations in polarized light are superior to the ordinary metallographic methods, largely dependent upon etching techniques.

Microstructure of β'.—Many photomicrographs of β' or "acicular β" have been published.* The appearance of this structure in polarized



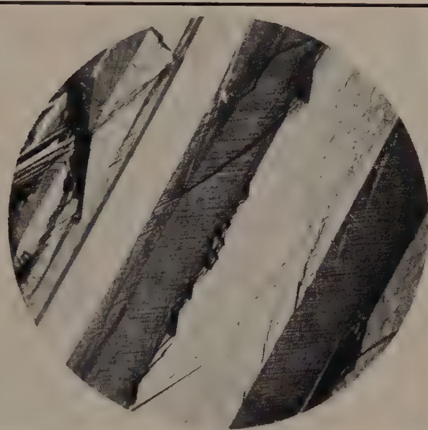


Fig. 3. Fig. 4.

Fig. 3.—β' martensite in an alloy of 13.2 per cent Al, cooled from 1000° C. in an air stream. × 125. Unetched.

Photographed with polarized light; analyzer 2° from crossed position. Rockwell B hardness, 84 to 88.

Fig. 4.—γ' martensite in an alloy of 13.6 per cent Al, quenched from 1000° C. in 10 per cent NaOH. × 125. Unetched.

Photographed with polarized light; analyzer 2° from crossed position. Rockwell B hardness, 100 to 102.

light is shown in Fig. 3. Polarized light studies indicate that β' martensite plates are arranged in parallel sets containing two (and only two) different orientations. Plates† of β' often contain small, usually irregular, cross bands (Fig. 3). Generally, the plate size of β' is larger the lower the speed of cooling from the β range.

Microstructure of γ'.—In polarized light, γ' differs from β' in that the γ' plates contain very fine parallel striations, which are suggestive of

* See, for example, Fig. 5, ref. 8.

† The gross structural unit of both β' and γ' will be referred to always as a plate; it is understood that the normal microstructural appearance of a plate must be that of a band.

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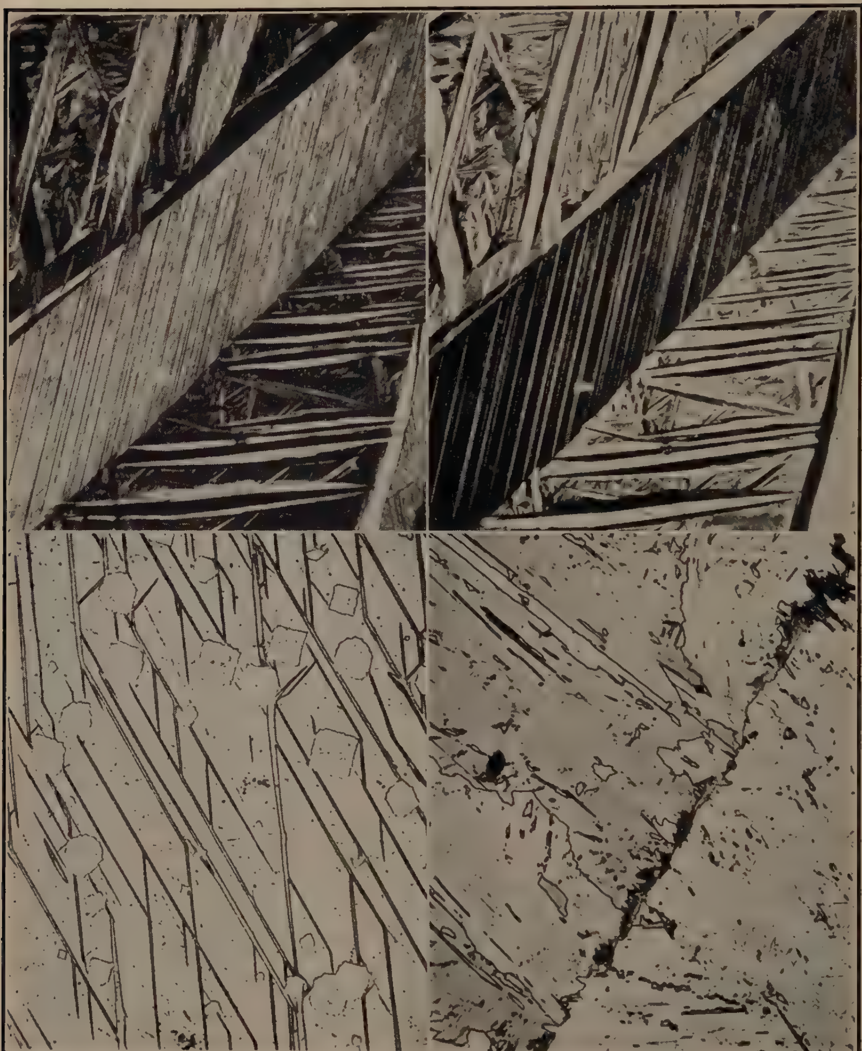

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FIG. 5.—γ' MARTENSITE IN AN ALLOY OF 13.6 PER CENT AL, QUENCHED FROM 1000° C. IN 10 PER CENT NAOH. × 165. UNETCHED.

Photographed with polarized light; analyzer 2° to the right of crossed position.

FIG. 6.—SAME AS FIG. 5, EXCEPT THAT ANALYZER IS 2° TO LEFT OF CROSSED POSITION.

FIG. 7.—14.7 PER CENT AL, QUENCHED FROM 1000° C. IN 10 PER CENT NAOH. × 300. ETCHED WITH $NH_4OH + H_2O_2$.

γ' plates and patches of δ in matrix of β_1. The color of β_1 after etching is brownish red.

FIG. 8.—9.3 PER CENT AL, QUENCHED FROM 1020° C. IN 10 PER CENT NAOH. × 100. ETCHED WITH $NH_4OH + H_2O_2$.

Massive α with traces of α reeds at grain boundary. Rockwell B hardness, 47 to 50.

twinning (Figs. 4, 5 and 6). These striations are most easily detected in large plates, but with care can also be seen in smaller plates. Inasmuch as the width of the striations decreases with the size of the plate containing them, and the efficiency of polarization decreases inversely with numerical aperture, it is not surprising that striations cannot be seen in the very smallest γ' plates. The γ' plates are often traversed by cross markings, which are considerably thicker and much more widely spaced than the striations.

Hypoeutectoid Alloys.—The structure of a metallographic specimen containing 9.3 per cent Al quenched from 1020° C. in 10 per cent NaOH is shown in Fig. 8; the crystal structure of this alloy is face-centered cubic. This type of microstructure (massive α) was first discovered by Phillips[16] in quenched Muntz metal. Slivers cut from this specimen and quenched from 1020° C. in NaOH had a β' microstructure; however, the Debye patterns of these slivers differed from the pattern of β' in that all weak lines of the β' pattern (notably, the first four lines of lowest θ values) were absent.* Evidently, the crystal structure of these slivers is the same as that of β' except that the atom arrangement is random instead of ordered; and therefore, the β phase of this composition does not undergo the ordering process during the quenching operation.

Hypereutectoid Alloys.—Fig. 7 illustrates the microstructure of an alloy containing 14.7 per cent Al quenched from 1000° C. in 10 per cent NaOH. An alloy of 15.4 per cent Al quenched from 1010° C. in 10 per cent NaOH consists entirely of δ. A discrepancy between the results of this study and that of Gawranek, Kaminsky and Kurdjumow[9] should be noted; namely, an alloy† of 13.2 per cent Al after both airstream cooling and quenching from the β range was found to consist entirely of β'.

Isaitschew's remarks (see p. 208) on the crystal structure of γ' were confirmed and extended. X-ray patterns obtained from quenched slivers containing 13.6 per cent Al had a line system in which all strong lines corresponded to a hexagonal close-packed lattice of $a_0 = 2.606$Å. and $c/a = 1.619$. The remaining lines (all relatively weak) were undoubtedly superlattice lines; no attempt was made to determine the type of ordering. Specimens of slightly higher aluminum content gave similar patterns except that many lines (but not the basal plane reflection) became doublets, and for a quenched specimen of 14.7 per cent Al, containing small amounts of γ', the splitting of (10.0) and (10.1) corresponded to about 1 per cent of their d values. This distortion of the hexagonal cell of γ' with increasing aluminum content is comparable in kind but not in degree to the well-known gradual change from cubic to tetragonal martensite in steel as the carbon content increases.

* For a list of β' Debye lines, see ref. 5.

† Both slivers and metallographic specimens. Duplicate chemical analyses were performed on two homogenized specimens; results: 13.22 and 13.20 per cent Al.

Decomposition of β', γ' and β_1 on Tempering.—Specimens of 13.2, 13.6 and 14.7 per cent Al were packed in graphite and homogenized in nitrogen atmosphere for 18 hr. at 1000° C., then quenched in water. Slivers were cut from these specimens and etched to about one-third of their original thickness. Slivers of 13.6 and 14.7 per cent Al were requenched from 1000° C. in 10 per cent NaOH. Slivers were then sealed in evacuated Vitreosil tubes, tempered, and the changes in structures after tempering were studied with rotation X-ray patterns. Results follow:

1. 14.7 *Per Cent* Al.—Original structure all β_1. X-ray patterns taken after seven days at 200° C. and after 14 days at 300° C. were the same; namely, structure was practically all δ (sharp shots) with faint smeary lines at positions corresponding to the strong lines of γ'.
2. 13.6 *Per Cent Al.*—Original structure all γ'. After 30 days at 200° C., a small amount of δ had formed; after 15 days at 300° C., the X-ray pattern showed γ' and δ (sharp spots) of about equal intensity. After 20 days at 350° C., γ' and δ are still present in about equal amounts, and the γ' spots are more sharply defined than those from as-quenched specimens.
3. 13.2 *Per Cent Al.*—Original structure all β'. Patterns after (1) 30 days at 200° C., (2) 14 days at 300° C., and (3) 20 days at 350° C. all look alike; that is, the structure remains unchanged except for the appearance of two very faint new lines, which could be α lines. Also, some of the β' lines have begun to merge, while others remain sharply defined. The β' lines that remain sharp are those that superimpose with lines on the γ' pattern, while for the pairs that begin to merge into single lines the pairs of β' lines correspond to single γ' lines. Apparently, then, there is a tendency for β' to transform into γ' on tempering. If the equilibrium state for all temperatures below the eutectoid is really $\alpha + \delta$, one should expect that 20 days at 350° C. would allow decomposition into substantial amounts of these two phases. This point warrants further study. In specimens that had been homogenized at 1000° C. for only 1 hr., both β' and γ' began to decompose more rapidly than they did in specimens homogenized for 18 hr. at 1000° C.

Deformation of β', γ', and β_1.—Mechanical deformation of either β' or β_1 results in transformation to γ'; only slight deformations are required to initiate this transformation, and with moderate deformation the transformation is complete. Deformation of γ' does not change its structure except for a noticeable reduction in intensity and eventual disappearance of the superlattice lines. γ' may also be formed from β_1 by liquid-air cooling. This transformation is not reversible; that is, γ' is still present after the specimen is brought back to room temperature.

Judging from these results, it appears probable that the cross markings observed in β' plates are strain-transformation markings[1] and that the cross bands in γ' are mechanical twin bands.

Orientation Habits of β' and γ' Martensite Plates

γ' Orientation.—The orientation habits of γ' plates with relation to the β_1 lattice were easily established. Specimens ($\frac{1}{2}$ in. dia. by $\frac{1}{4}$ in.) of 14.7 per cent Al, after quenching in 10 per cent NaOH from 1000° C. contain β_1, γ', and δ (Fig. 7). After this structure was produced, two surfaces were prepared on each specimen and the poles of γ' plates were located stereographically with respect to a surface and the common edge.[14] The specimen was then deeply etched, and the orientation of the β_1 lattice was determined to within $\frac{1}{2}$° or less by means of the back-reflection Laue X-ray method;[15] this orientation was then plotted on the stereographic projection containing the γ' poles. The over-all inaccuracy

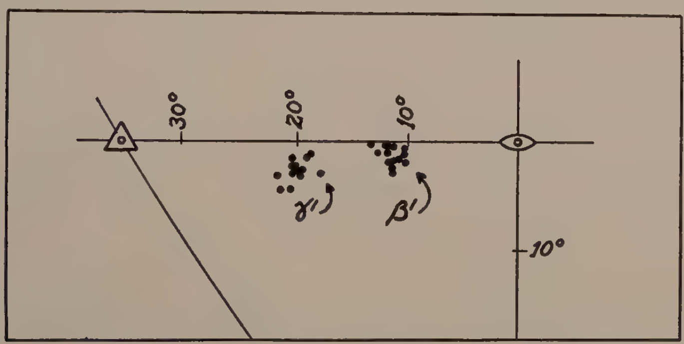

Fig. 9.—Stereographic projection of β' and γ' martensite poles plotted on standard {110} of matrix lattice

Only a portion of one of the stereographic triangles is shown. Oval = $\{110\}\beta_1$; triangle = $\{111\}\beta_1$.

in the method is estimated at about 1°. Results obtained from four grains in three different specimens are summarized stereographically in Fig. 9.

β' Orientation.—β' and β_1 cannot be obtained together in a specimen at room temperature; hence, a complete solution of the orientation habit of β' requires that the orientation of the β_1 matrix lattice be determined above the martensite transformation temperature. Because of the high corrosion resistance of these alloys, specimens may be heated in air during the X-ray exposures; atmospheric protection is unnecessary.

For this work, a 75-watt electric resistance furnace capable of maintaining a small specimen at temperatures up to 600° or 700° C. during the X-ray exposure was constructed. The Nichrome winding was mounted in a cylindrical Transite frame, and surrounding the winding and insulated from the frame was a shell of aluminum bronze (top end closed), which served as heat conductor and specimen holder. One end of the specimen was inserted into a hole at the top of the aluminum bronze shell and was held firmly in contact with the shell by means of a set screw. The entire

unit was mounted on a back-reflection Laue X-ray camera in such a way that the specimen-to-film distance (3 cm.) and the specimen orientation could be accurately adjusted. A fine-wire thermocouple was inserted into a small hole drilled in the specimen and the temperature of the specimen was controlled with a Variac transformer connected in series with the Nichrome winding.

The procedure used in evaluating the orientation habit of β' plates was as follows: A specimen of 13.2 per cent Al (cooled from 1000° C. in an air blast) was polished on three surfaces and the locations of several β' plates were measured microscopically. The specimen was then deeply etched and placed in the high-temperature holder described above. The temperature was raised to 400° C., then lowered to about 320° C., and was held here during the X-ray exposure (3 hr.). The resulting Laue patterns were rather faint; nevertheless quite satisfactory for orientation work. Matrix orientation and martensite poles were plotted stereographically in the usual manner. Results obtained from the two specimens studied are summarized in Fig. 9.

After the β'-β_1 lattice relationship had been evaluated (see next section), a determination of a β_1 crystal orientation could be arrived at through the measured orientations of two β' plates contained in that crystal. This method was used on a specimen of 12.5 per cent Al, and the three poles thus located fell within the same stereographic region that is shown for β' in Fig. 9.

Lattice Relationships

In the evaluation of lattice relationships between two phases in an alloy, a complete solution for any general case is possible only when the orientation of a single crystal of one phase can be determined and compared with the orientation of a single crystal of the other phase. Unfortunately, the crystal sizes of phases that result from lattice transformations are practically always too small for a complete solution to be possible, and one is forced to resort to some indirect method of study involving assumptions of one type or another, which necessarily detract from the value of the final result. Pole-figure methods, for example, yield an integrated result from many crystals, therefore an approximation, and provide an inadequate reply to the question: Are the deviations from ideal lattice relationships, so often observed, merely incidental, or are they real? It appears that an answer to this question, especially with reference to one or two martensite transformations, is greatly to be desired, and must be obtained before postulations of specific transformation mechanism can be regarded as anything but pure speculation.

Fortunately, the plate size of both β' and γ' copper-aluminum is sufficiently large* in high-purity alloys to render feasible a complete

* The thicknesses of the largest plates of β' and γ' were about 0.1 mm.; only in two or three observed cases did this thickness reach a value of 0.2 mm.

solution of lattice relationships. After some time had been spent in developing a technique, it was possible to grind and polish a specimen of β' or γ' martensite on a surface parallel to an individual plate, and thus to expose (after etching) a single martensite crystal for an area of 1 to 2 mm. The spots on back-reflection Laue X-ray patterns so obtained from these crystals, especially those from γ', were surprisingly sharp and free from distortion. In so far as one may judge from these Laue patterns, the perfection of the γ' martensite lattice equals that of the β_1 lattice from which it is formed.

The γ'-β_1 Lattice Relationships.—Preliminary work performed on specimens containing 13.6 per cent Al quenched from 1000° C. into 10 per cent NaOH yielded the following results:

1. Every back-reflection Laue pattern from a plate of γ' showed the presence of not one but two hexagonal close-packed lattices. These two orientations are always related in exactly ($\pm 1/5°$ or less) the same way: The relationship is that of twinning on (10.1) and always on the same (10.1) plane. These two twinned orientations contained in a "single" γ' plate will be referred to as A_1 and A_2, respectively. The relative spot intensities A_1:A_2 varied from about 2:1 to 1:1.

2. Previous microscopic studies had shown (see p. 209) that γ' plates were arranged in parallel sets containing two obviously different orientations (corresponding to the light and dark broad bands of Fig. 4). X-ray work confirmed this observation, for in addition to the A_1 and A_2 orientations contained in one plate, a second set of twinned orientations, B_1 and B_2, was found in the plate adjacent and parallel to the first one. Thus, with reference to the γ' microstructure shown in Fig. 4, A_1 and A_2 are two orientations contained, for example, in the plates represented by the light broad bands, and B_1 and B_2 in plates represented by the dark broad bands.

3. After several sets of A and B orientations in specimens of 13.6 per cent Al had been determined and plotted stereographically, it was possible to deduce the relationships between these γ' orientations and the orientation of the matrix lattice. However, in order to complete the solution, similar studies were made on two specimens of the 14.7 per cent Al alloy, which contained (after quenching from 1000° C. in NaOH) large γ' plates in a matrix of retained β_1. A surface was ground and polished along a set of parallel martensite plates, exposing areas of γ' and β_1 on the same surface. After determining the orientation of A_1 and A_2 in one martensite plate, the specimen was translated parallel to the film (on the X-ray camera) and in turn the B orientations of γ' and the orientation of the β_1 crystal were determined. The results from both specimens studied were in perfect agreement; likewise in agreement with the solution suggested by the work on the 13.6 per cent Al alloy. The over-all inaccuracy of the above operation is estimated at $1/4°$ to $1/2°$.

The γ'-β_1 lattice relationships are summarized stereographically in Fig. 10. In this figure are plotted the important poles of the body-centered cubic β_1 lattice with the plane of projection as the surface of polish (parallel to a set of martensite plates). Likewise plotted are the basal plane poles of the four γ' orientations contained in plates parallel to the polished surface, as well as the poles of the two active (10.1)

FIG. 10.—ORIENTATION RELATIONSHIPS BETWEEN LATTICES OF γ' AND MATRIX β_1. Projection shows basal planes and active twinning planes of the four γ' orientations contained in one set of parallel martensite plates. Plane of projection is plane of set of martensite plates. Great circles represent close-packed directions common to both lattices. Ovals, squares and triangles are poles of body-centered cubic β_1 lattice.

twinning planes. The great circle passing through (00.1) of A_1 and (00.1) of A_2 represents the close-packed direction $[01.0]_{\gamma'}$ which is common to both A_1 and A_2, and which is parallel to the close-packed direction $[1\bar{1}1]_{\beta_1}$ in the body-centered cubic lattice. An equivalent common direction is shown for B_1 and B_2 orientations. Crystallographically, the γ'-β_1 lattice relationships may be defined as follows:

$$\left.\begin{array}{l}(00.1)_{\gamma'} /\!/ (110)_{\beta_1} \\ [01.0]_{\gamma'} /\!/ [1\bar{1}1]_{\beta_1}\end{array}\right\} A_1 \text{ (or } B_1)$$

$$\left.\begin{array}{l}(00.1)_{\gamma'} : (011)_{\beta_1} = 4^\circ \\ [01.0]_{\gamma'} /\!/ [1\bar{1}1]_{\beta_1}\end{array}\right\} A_2 \text{ (or } B_2)$$

A_1 and A_2 are twins, with twinning plane (10.1); that is, orientation A_2 may be produced from A_1 by a rotation of 180° about the normal to (10.1).

It appears quite safe to conclude that the fine cross striations in γ' plates revealed by microscopic studies with polarized light (Figs. 5 and 6) are actually twin striations, and that this twinning is probably a part of the transformation mechanism. For if it were argued that A_1 represents the basic product of the transformation, twinning could produce six new orientations, whereas experimentally we find only one of the six possibilities and, furthermore, always the same one. Also, the twinning law for γ' differs from the only one heretofore established for hexagonal close-packed metals and alloys,[18] which twin on (10.2).

The β'-β_1 Lattice Relationship

A complete solution of the crystal structure of β' is not yet available. Considerable information has been obtained from back-reflection Laue patterns and oscillating crystal patterns, but the picture is yet far from complete. The main obstacle to a straightforward solution is the fact that the orientation of β' lattice with respect to the β' plate is always the same; hence only a limited region of the lattice projection can be properly covered. The Laue symmetry is pseudoholohedral trigonal, but so far it has not been possible to establish with certainty just how the true symmetry departs from holohedral trigonal. The available data on crystal structure pertinent to the present problem of lattice relationships are as follows: The lattice is layerlike, with a framework resembling that of γ', and the three important directions in the basal plane are at angles of 60° ($\pm\frac{1}{2}$°) to one another; the angle between [00.1] of the pseudohexagonal framework and the basal plane is 89° ($\pm\frac{1}{2}$°).

Back-reflection Laue X-ray studies were carried out on specimens of 12.6 and 13.2 per cent Al, which had been cooled from 1000° C. in an air stream. In agreement with the results of microscopic work, the X-ray studies showed that β' plates are arranged in parallel sets containing two different orientations and each plate is a single crystal; i.e., β' plates are not twinned. These two orientations will be referred to as A and B, respectively. After several pairs of A and B orientations had been determined in specimens of 12.5 per cent Al, and the relationship of A to B had been examined stereographically, the lattice relationship could be predicted with considerable assurance. However, in order to complete the solution, a specimen (13.2 per cent Al) sized to fit the high-temperature specimen holder (see p. 213) was prepared. With the specimen mounted in this holder, the A and B orientations of the exposed β' plates were first determined at room temperature; then the specimen temperature was raised and the orientation of β_1 was determined at about

340° C. The results so obtained agreed with the relationship that had previously been predicted, and are shown stereographically in Fig. 11. The method of plotting is the same as that used for the γ'-β_1 relationship. In this figure, the great circle passing through the pole of the basal plane of A represents the close-packed direction in the basal plane that is parallel to the close-packed direction $[1\bar{1}1]_{\beta_1}$ of the body-centered cubic lattice. An equivalent direction common to the B orientation of γ' and

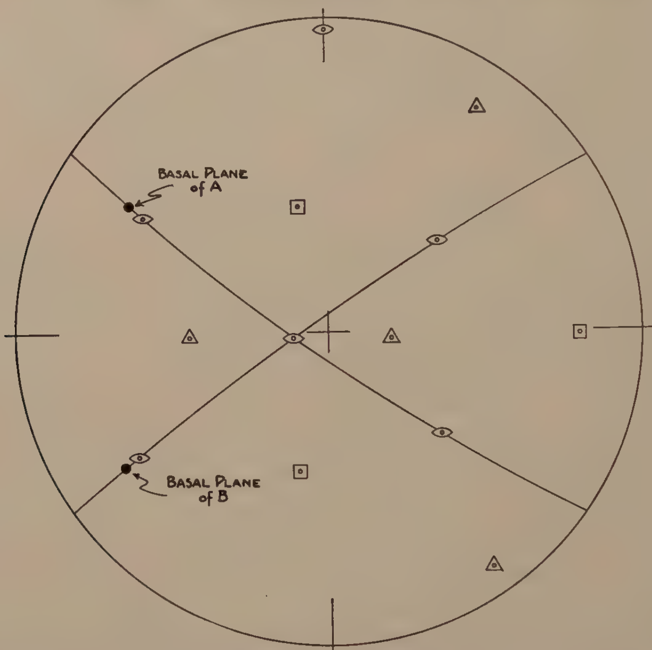

FIG. 11.—ORIENTATION RELATIONSHIPS BETWEEN LATTICES OF β' AND MATRIX β_1. Projection shows basal planes of the two β' orientations contained in one set of parallel martensite plates. Plane of projection is plane of set of martensite plates. Great circles represent close-packed directions common to both lattices.

the lattice of β_1 is also shown. The basal planes of γ' and $\{110\}$ of β_1 are not parallel but are separated by an angle of 4°.

DISCUSSION OF RESULTS

An obvious gap in the foregoing series of data on this martensite transformation is the lack of a complete solution to the crystal structure of β'. One wishes that it were possible to plot the atom positions of β' and β_1 and to compare these in terms of their known orientation relationships, for such a comparison, when made, may indeed be the starting point to an understanding of orientation habits and thus of metallographic structures in general. For the time being, no attempt will be made to correlate habits with orientation or to hypothesize on the martensite

mechanism; discussion will be limited mainly to emphasizing certain facts among the data already presented.

The β' orientation habit, except for scatter, is the same as that of β' in the copper-tin system;[1] namely, about 2° from $\{133\}_{\beta_1}$. The Debye patterns of these two β' phases are similar but by no means identical. The stereographic region defined by γ' poles is about 3° removed from $\{122\}_{\beta_1}$. γ' has no known counterpart in other alloy systems, although the martensite in steel might very well be considered as an equivalent phase of different crystal structure, for the behaviors of these two are in many ways similar.

For both γ' and β', lattice relationships were found to be considerably more accurate and consistent than orientation habits. A single crystal of β_1 may produce a maximum of 36 γ' orientations, of which 12 will be A_1 orientations and 24 will be A_2 orientations. It is an interesting fact that the 24 A_2 orientations of γ' are exactly the same (in so far as location of basal plane and directions within that plane are concerned) as the 24 orientations of β' that may be obtained from a single crystal of β_1; for both lattices, a close-packed direction is parallel to $[1\bar{1}1]_{\beta_1}$ and the basal plane is at an angle of 4° to $(110)_{\beta_1}$. These two cases differ, however, in the angles made by the basal plane and the martensite plate. The angles between the plane of a martensite plate and the basal plane of the lattice contained in the plate are (approximately) as follows:

For the A_1 orientation of γ'	78°
For the A_2 orientation of γ'	27°
For the B_1 orientation of γ'	82°
For the B_2 orientation of γ'	28°
For the A orientation of β'	74°
For the B orientation of β'	76°

Of extreme interest is the question of interrelation among the two martensite lattices and the equilibrium phases α and δ. Since β' transforms to γ' on being deformed and at least tends to transform to γ' on tempering, it might be considered transitional to γ'; also, γ' is the more easily decomposed of the two. This behavior of β' and the behavior of β_1 on tempering suggests that there must be a hexagonal close-packed equilibrium phase (equivalent to the Cu_3Sn in the copper-tin diagram) stable only at temperatures near room temperature. It would, of course, be next to impossible to prove this point, if the homogeneity range of the phase does not extend greatly above room temperature.

In possible conflict with the above assumption stands the puzzling but nonetheless rather definite intimacy between γ' and δ, which is demonstrated by the behavior of γ' on tempering. It is truly remarkable that a γ' specimen containing 36 possible orientations twinned on such a fine scale should transform, on tempering, into a single orientation of δ. This fact can be explained in only two ways. Either the transformation

to δ is nucleated* by small traces of retained β_1 (or β') that are undetected by X-ray or microscopic methods, or else the transformation $\gamma' \rightarrow \delta$ is a crystallographic reversal of the transformation $\beta_1 \rightarrow \gamma'$.

The latter view would fit in nicely with the origin of the γ' twin striations suggested by crystallographic reasoning (see p. 217); that is, these twin striations would be considered as resulting from the transformation mechanism $\beta_1 \rightarrow \gamma'$ and as vanishing with the reversal transformation mechanism $\gamma' \rightarrow \delta$. However, it is not possible at this time to reject with certainty either of the hypotheses outlined above.

In so far as origin is concerned, the twinning of γ' may be regarded as analogous to the transformation twinning of α iron.[17] This fine-scale twinning greatly decreases the effective grain size and (as adjacent basal planes are at angles of 56° to one another), undoubtedly contributes materially to the high hardness of γ' martensite.

Summary

An X-ray and microscopic study of the martensite transformation in β copper-aluminum alloys of compositions between 9.3 and 15.35 per cent Al has been made. The following orientation relationships have been accurately evaluated for both β' and γ' martensite:

1. The orientation of the martensite plate in relation to the matrix β lattice (Fig. 9).
2. The orientation relationships between the martensite lattice and the matrix β lattice (Figs. 10 and 11).
3. The orientation of the martensite lattice in relation to the plane of the martensite plate (Figs. 10 and 11).

In addition, the following new observations regarding transformations in β copper-aluminum alloys were made:

1. An alloy of 9.3 per cent Al rapidly quenched from the β range undergoes "mass transformation" to α.
2. If this alloy is quenched even more rapidly, the resulting structure is similar to β' except that the atom arrangement is disordered instead of ordered.
3. As the aluminum content is increased (from 13.6 to 14.7 per cent Al) the hexagonal close-packed lattice of γ' becomes slightly distorted. This distortion is likened to the change from cubic to tetragonal martensite in steel as the carbon content increases.

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* It is well known that for the reaction: body-centered cubic $\rightarrow$ γ-brass structure, the cubic axes of the two lattices are parallel (see refs. 7 and 10).

The complete reversibility of single crystal β back to the identical single-crystal orientation (for any kind of cooling and heating cycle) was observed in all alloys except those of compositions of 10 per cent Al or less. In the latter, tempering (after quenching) results in transformation from disordered β' to α, and the subsequent transformation of α to β at higher temperatures produces a set of β grains (visible, of course, after quenching) different from the original set.

4. The striations in γ' martensite are shown by X-ray studies to be due to polysynthetic twinning on (10.1).

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DISCUSSION

(R. M. Brick presiding)

G. KURDJUMOW,* Dnepropetrowsk, U. S. S. R. (written discussion).—The author indicates that the γ' hexagonal lattice becomes distorted when there is an increased content of aluminum. This distortion, it seems to me, may be explained by taking into consideration the arrangement of copper and aluminum atoms in the γ' lattice. The determination of the γ' superlattice has shown that identical atoms are arranged not in the form of a hexagonal but of a rhombic lattice belonging to the space group D_2h^{13}. The arrangement of atoms Al and Cu in the γ' lattice was first calculated by us and then checked experimentally.[21] Our calculation was based on the following considerations: Transformation $\beta_1 \rightarrow \gamma'$ belongs to the martensite type of transformations. Lattice β_1 is known and has an ordered arrangement of atoms. If our ideas on martensite transformations are correct, and if they really represent transformations during which an ordered rearrangement of the lattice takes place without any interchange of places among the atoms, lattice γ' must also have an ordered arrangement.

In a previous investigation we determined the orientation of the γ' lattice axes in relation to the axes of the lattice. The author's data are in perfect agreement with our results.

On the basis of this determination a scheme for the diffusionless transition $\beta_1 \rightarrow \gamma'$ has been proposed analogous to the Burgers's scheme[22] for the transition of the body-centered cubic lattice into the hexagonal close-packed lattice.

From the knowledge of the coordinates of atoms Al and Cu in the β_1 lattice, and taking into account the proposed mechanism for the transition under consideration, it was possible to calculate the atom coordinates on a hexagonal lattice.† The arrangement of identical atoms (e.g., Al) found in this way proved to be without any hexagonal axis and having only three twofold perpendicular axes coinciding with directions [11.0], [11.0] and [00.1] of the hexagonal lattice. Lattice γ' can be described with the following coordinates:

$$\mathrm{Al}\begin{Bmatrix} 0 & 0 & 0 \\ \frac{3}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \qquad \mathrm{Cu}\begin{Bmatrix} \begin{pmatrix} 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & \frac{1}{4} & 0 \\ \frac{1}{2} & \frac{3}{4} & 0 \end{pmatrix} & \begin{pmatrix} \frac{1}{3} & 0 & \frac{1}{2} \\ \frac{5}{6} & \frac{1}{4} & \frac{1}{2} \\ \frac{5}{6} & \frac{3}{4} & \frac{1}{2} \end{pmatrix} \end{Bmatrix}$$

The lattice constants of an alloy with a 13.5 per cent content of aluminum are $a = 4.51$ Å., $b = 5.20$ Å., $c = 4.22$ Å. A calculation of the structural factor shows that the lattice must give a great number of weak superlattice lines. The checking has been done with the aid of a β-phase single crystal (14 per cent Al), which on quenching was transformed into γ'. The calculation interference spots for 18 lattice planes giving superlattice spots were discovered at the required Bragg's angles of reflection and at the required angles between the normals to lattice planes and the axis of rotation of the crystal. The coincidence between the calculated and experimental results confirms our views concerning the mechanism of martensite transformations.

Notwithstanding the fact that identical atoms possess a rhombic symmetry, all lattice seats (occupied by copper and aluminum atoms) belong to the hexagonal, close-

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* Physical Technical Institute.

[21] G. Kurdjumow and V. Miretzky: *Jnl. Tech. Phys.* (1938) No. 22. In Russian.

[22] W. G. Burgers: *Physica* (1934) **1**, 561.

† Compare with calculation of atom coordinates in the α' lattice of copper-zinc alloys.[23]

[23] E. Kaminsky and G. Kurdjumow: *Metallwirtshaft* (1936) **15**, 905.

packed lattice. It is natural to expect that with a change in the aluminum content the arrangement of all the lattice seats will take a rhombic symmetry according to the symmetry of identical atoms.

I should like to ask the author if the interference picture in the case of aluminum content discovered by him could not be described in the terms of the rhombic lattice.*

The author's data concerning the nonreversibility of the transformation agree with our previous results.[24] However, the possibility of a big hysteresis discovered during the $\beta_1 \leftrightarrows \beta'$ transformation[25] obliged us to reconsider the question and start supplementary experiments. The latter showed that the transformation $\beta_1 \rightarrow \gamma'$ is reversible but is accompanied by a big hysteresis. In an alloy with a 13.3 per cent content of aluminum the transformation $\beta_1 \rightarrow \gamma'$ in our alloys takes place at temperatures of about 200°. On heating, the reverse transformation $\gamma' \rightarrow \beta_1$ takes place in a temperature region near 350°. Transformation $\gamma' \rightarrow \beta_1$ could be discovered in this alloy only when the heating was conducted rapidly, before the diffusion decomposition of the γ' phase[26] took place.

Besides, the alloy with a 14.5 per cent content of aluminum, which on quenching has a β_1 lattice, was photographed at room temperature, at liquid-air temperature, and again at room temperature. This alloy showed[26] a complete reversibility of $\beta_1 \rightarrow \gamma'$ transformation. On the basis of available data, it is possible to consider that martensite transformations that pass in a pure state without processes of diffusion must in general be reversible.[27]

The reasons why our data concerning the concentrations of aluminum at which the γ' lattice appears are not in accord with the author's data on this subject are not quite clear to me; possibly, these divergencies are caused by a different contamination. I should like to mention here that the delicate experiments on the structure of separate β' and γ' laminae, so excellently conducted by the author, open new ways for the further study of martensite transformations.

I. Isaitschew† and I. Salli,† Dnepropetrowsk, U. S. S. R. (written discussion).—The author indicates that "γ' may also be formed from β_1, by liquid-air cooling. This transformation is not reversible; that is, γ' is still present after the specimen is brought back to room temperature."

In a preceding discussion, we wrote of our having observed a similar phenomenon in copper-tin alloys with a 25 per cent content of tin. When a sample quenched from the β region in water is immersed into liquid air, the β phase is transformed into a new phase of the martensite type, which remains unchanged at room temperature.

A more detailed study of this phenomenon has shown that the martensite phase begins to appear at temperatures considerably higher than the temperature of liquid air (approximately minus 40° C.), but very little of it forms at these temperatures. As the temperature drops, the martensite phase increases.

At the temperature of liquid air, part of the β phase still remains untransformed. On heating to +100° C. a sample in which transformation into the martensite phase at low temperature has already taken place, the amount of martensite phase remains practically unchanged. Heating to +200° C. causes a noticeable decrease of the

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* In this case indices (120) to (200) should be attributed to the split line (100), and indices (201) and (121) to the double line (101).

[24] G. Kurdjumow and T. Stelletzkaja: *Tech. Phys.* U. S. S. R. (1935) **2,** 1.

[25] V. Gridnew and G. Kurdjumow: *Tech. Phys.* U. S. S. R. (1938) **4,** 1.

[26] G. Kurdjumow and V. Miretzky: *Jnl. Tech. Phys.* (1938) **8,** 1777. In Russian.

[27] Following discussion by I. Isaitschew and I. Salli.

† Physical Technical Institute.

martensite phase; on heating at a rapid rate to 350° C. and then quickly cooling, a pure β phase was obtained. The presence of phases was verified by X-ray patterns.

From these facts, it may be seen that in copper-tin alloys the temperature hysteresis is very great; it exceeds 400° C., and room temperature lies in this interval. Notwithstanding such a great temperature hysteresis, the transformation process seems to be reversible.

The $\beta_1 \rightarrow \gamma'$ transformation in copper-aluminum alloys belongs to the type of martensite transformations; consequently, if the converse transition $\gamma' \rightarrow \beta_1$ does take place, it must proceed at higher temperatures than the transition $\beta_1 \rightarrow \gamma'$. It is difficult to say how large is the magnitude of the temperature hysteresis in the alloys investigated by the author, but apparently room temperature lies inside it. Accordingly it may be supposed that if the author had heated the γ' phase to higher temperatures, transition $\gamma' - \beta_1$ would have occurred. This assumption is the more probable because the reversibility of the $\beta_1 - \gamma'$ transformation was already observed by Kurdjumow and Miretzky.[26]

It is advisable to make the heating fairly rapid, as there is always danger of the γ' phase beginning to decompose before it passes into β_1, owing to diffusion processes.

The reversibility of martensite transformations in eutectoid alloys is apparently a general property of all transformations of this type. We may ask how complete is the reversibility in such transformations? It is natural to expect that the higher the temperature of the converse transition, the greater are the possibilities of diffusion processes occurring and, consequently, of stable phases precipitating. The formation of stable phases can affect the further course of transformations in two ways: (1) the formation temperature of the martensite phase may drop considerably, and become lower than the temperature used in experimenting; (2) the precipitated stable phases may take such a disposition in the solid solution as to hinder the sudden reconstruction of the lattice.

During the first stage of precipitation, it is difficult to notice the new phases by means of the X-ray method, but at the same time the transformation process (solid solution $\leftrightarrows$ martensite phase), will be delayed.

For instance, X-ray patterns of a rotating β-phase single crystal with a 25 per cent content of tin obtained prior to the martensite transformation and subsequently (rapid heating to 350°) were identical; but subsequent immersions into liquid air did not cause any appearance of the martensite phase; but the transformation takes place if we quench the sample once more from the β-phase region. It is possible that the worse reversibility after a number of cycles may take place also when the transformations occur at about room temperature, owing to lattice distortions.

It is also possible that with the increase of the number of distortions in the lattice—i.e., of the number of transformation cycles—the temperature hysteresis will also increase. It is to be regretted that there are no experimental data on this point and that therefore it can be discussed only theoretically.

M. G. Corson,* New York, N. Y. (written discussion).—A metallurgical paper must either be limited to a strictly technical field or else form a distinct and precise contribution to the science of metals, such as will enrich other metallurgists' background. To do this it must present at least a clear-cut picture of the subject studied, although to be of real value it should contain a theory of the process involved and a correlation of the subject with other physical characteristics. The present paper fails to measure up to these objective requirements.

Metallurgists working with copper-base alloys containing the beta phase (straight betas are not used) know that the increase in the amount of beta causes a loss of

* Consulting Metallurgist.

ductility and a great increase in hardness. Except for beta brasses, in which the beta does not undergo a drastic change, the high hardness and brittleness of the former "beta" at low temperatures cannot be much altered by varying the heat history of the alloy. Anneal it, quench it, temper it as you wish, but a copper-aluminum alloy with over 11.5 per cent Al will remain nearly as hard and as brittle (unless it contains a great deal of iron). In addition the electrical conductivity also remains practically unchanged, indicating that the cold alloy must represent a body of rather constant ratios between its various constituents.

In addition, the true beta is extremely soft and plastic, and the loss of plasticity plus hardening on cooling from the beta range ought to be caused by a *thorough structural* change.

But the present author and those whom he mentions believe that we have in all cases (up to 13.2 per cent + to be sure) merely different varieties of beta. One is distinguished by the "orderliness" of its structure as seen by the X-rays, plus certain "superlattice lines." The other β' appears "acicular" under the microscope. However, the author does not present his X-ray spectrograms and calculations that might show where the analogies and the differences between the three varieties of beta really lie.

The reference to the "acicular" structure means merely an adherence to the ideas of old times when every self-respecting metallurgist simply had to establish the existence of a new type of a "phase," to wit: troostite, sorbite, osmondite, ledeburite, which are not phases at all but mere mixtures in varying (and continuously varying) degrees of dispersion. The "acicular" phases were taken on in a particularly eager manner because the structures looked similar to bundles of needles or cross sections of packages of plates. However, the similarity is very remote. It does not hold true even for the martensite in steel, and much less so in quenched beta copper alloys. To an unprejudiced eye the "acicular" structure means "needles or plates" *profusely distributed through some other matrix.*

On page 212 the author discusses the structures obtained by quenching and by further tempering in three hypereutectoidal compositions, and obtains: (1) Al, 13.2 per cent; original structure (as quenched? The point is not clear.), β'. (2) Al, 14.7 per cent; original structure β_1. (3) Al, 13.6 per cent; a composition intermediate in its aluminum content and much closer to the first alloy. One would expect to find a mixture of β' with β_1, the first predominating. Instead the author gets "all γ'."

One might expect the 14.7 per cent alloy, which has to pass on its way to low temperatures through a binary field (beta plus gamma), to retain some gamma and to change it to another variety of gamma. (The differences between γ and γ' are not mentioned.) But how this might occur in the 13.6 per cent alloy without occurring in the 14.7 per cent alloy, notwithstanding the fact that the 13.6 per cent vertical nowhere comes close to a gamma region, I cannot understand.

Does the author really intend to say that he obtained a definite improvement by using "polarized" light in his micrographic studies? Are we to believe that polarized light can tell anything about the structure of a flat, defectless metallic surface? The author shows some beautiful pictures, but the reason is that he used "oblique"* light and his Figs. 5 and 6, taken at a symmetrical obliquity, show what could be expected: dark becomes bright and bright becomes dark. The conical stop illumination proposed by H. George some 15 years ago would do exactly the same. To corroborate my last objection I wish to reproduce here a picture (Fig. 12) of the structure of a 12.5 per cent aluminum bronze as it appears in Fig. 87, plate XI, of the little book by H. Behrens, "Das mikroskopische Gefuege der Metalle und Legierungen,"

* 2 per cent off the crossed position.

published in 1894. At that time metallography was in its infancy. The microscopes were crude, illumination poor and aluminum bronze a mere curiosity. There was no microphotography. The picture shown was sketched by hand and reproduced as a wood cut. The sample was not specially heat-treated. Nevertheless the analogy with Dr. Greninger's Fig. 3 is most striking. No polarized light was used.

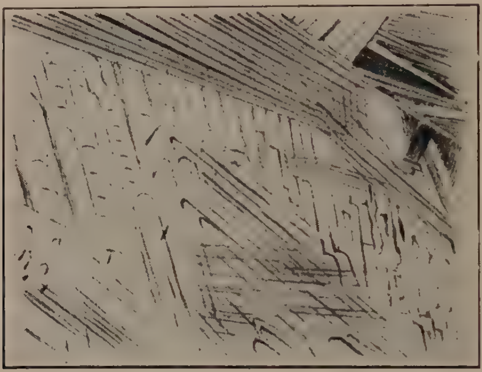

FIG. 12.—STRUCTURE OF ALUMINUM BRONZE AS SKETCHED BY H. BEHRENS.

I believe strongly in the usefulness of polarized light when studying special details (mainly nonmetallic inclusions), but its limitations must be clearly understood.

"Ten thousand times the critical cooling velocity" (page 204, line 4 from the bottom). To this statement I object because it is so misleading. The critical velocity is by no means low itself and not so easy to measure for that very reason. How would one measure cooling velocities ten thousand times greater?

I wish to present now my own conceptions of the changes that occur in beta copper alloys on cooling below the transitional lines and the eutectoidal isotherm, leaving highly hypereutectoidal alloys out of consideration for the time being. The eutectoidal transformation cannot be prevented. In every case a mixture of alpha plus delta plus a certain amount of undecomposed beta* results and the ratios of the three phases are nearly identical whether the alloy is annealed, quenched or tempered. *That is why the final hardnesses and conductivities do not vary much.* The size, shape and habit of aggregation of the products of the eutectoidal dissociation may differ vastly. In the extreme case the mixture of the daughter phases may form an ultramicroscopic pseudomorphose in the shape of the mother phase (β). In less extreme cases it may look "acicular," troostitic, pearlitic or show clearly divorced phases. In some of them X-rays will reveal new lattices; in others we shall get neither precise nor constant lattices of the β' type. Whether an X-ray specialist may be able to refute the proffered theory as "utterly impossible" and to prove the refutation mathematically, I do not know. I know, however, that this theory explains the hardness, brittleness and sameness of conductivity in the low-temperature products of the beta

* My statement regarding the nearly constant ratios of alpha : delta : residual beta contradicts the phase theory. A situation of this kind is not theoretically possible in a heterogeneous system, although it would hold its ground firmly for a homogeneous system (reaction constant). I suggest here that alloy systems in certain states of subdivision may be considered as occupying an intermediate status—neither definitely heterogeneous nor fully homogeneous, and that at the short distances between the elementary particles of the phases present (particularly in quenched alloys) a variant of the reaction-constant law may come into play.

phase, while the mere and vague statement of the existence of the β' and β_1 does not do so.

A. B. Greninger (written discussion).—Messrs. Kurdjumow, Isaitschew and Salli have supplied some valuable and extremely welcome information on the reversibility of $\beta_1 \rightarrow \gamma'$ CuAl and of $\beta \rightarrow \beta'$ CuSn. Certainly, this complete crystallographic reversibility, which may well be common to all martensite transformations when diffusion processes can be suppressed, constitutes one of the most appealing problems for study in this field. Apparently, the only martensite transformation for which reversibility has not been established is the martensite transformation in iron-carbon alloys. Here, a demonstration of reversibility may be extremely difficult if not impossible, because of the high velocity at which iron-carbon martensite decomposes; this decomposition proceeds at a measurable rate even at room temperature, and at temperatures near 400° C. decomposition is complete in a small fraction of a second. It will be recalled that several years ago, Wassermann[28] demonstrated the reversibility of the martensite transformation in alloys of iron and nickel; and we have recently substantiated Wassermann's conclusions while studying the martensite transformation in an alloy of iron + 32.5 per cent nickel. In this alloy, the reversible transformation is also accompanied by a large hysteresis, amounting to about 400° C. or more.

With the new information on the reversibility of $\beta_1 \rightarrow \gamma'$ CuAl supplied by Professor Kurdjumow, it is now possible to explain the "peculiar" behavior of γ' on tempering—commented upon on page 219. Inasmuch as reversibility does occur at 350° C., it is possible that the crystallographic behavior of γ' on tempering at any lower temperature can be linked with the reverse transformation $\gamma' \rightarrow \beta_1$ in that this transformation probably precedes the decomposition into the equilibrium δ phase.

It is quite possible that the distortion of the γ' lattice with increasing aluminum content may be due to a gradual change to a lattice of rhombic symmetry. However, quantitative work on this structure would be very difficult because the splitting of the lines is very small and the patterns we have obtained so far show the Debye lines to be not at all sharp. It is possible to state that for at least a limited range of θ the frequency and disposition of lines is not in disagreement with the postulated rhombic lattice, but for substantiation we should need additional systematic study of this structure.

Kurdjumow and Miretzky are to be complimented on their success in deducing the correct unit cell and atom positions of γ' by applying theories of lattice transitions; and their results must be regarded as confirmation of the view that martensite transformations do not involve diffusion. It is not so certain, however, that the mechanism of lattice transformation proposed by Burgers can be regarded as substantiated.

The space available for my reply makes it impossible for me to go into sufficient detail to promise the possibility of a better agreement with Mr. Corson.

[28] G. Wassermann: Ueber den Mechanismus der Umwandlung des Eisens. *Mitt. K. W. Inst. Eisenforschung* (1935) **17**, 149–155.

Effect of Silver on the Gold-copper Superlattice, AuCu

By Ralph Hultgren,* Member, and Lester Tarnopol,† Junior Member A.I.M.E.

(Detroit Meeting, October, 1938)

A considerable interest in the subject of superlattices has been manifested by many papers and reviews that have recently appeared, both in physical and metallurgical publications. This interest is due largely to the apparent simplicity of the ordering process, which permits the explanation of many phenomena on the basis of elementary theory. Moreover, ordering may cause important changes in the physical properties of alloys.

In this paper, we shall discuss the causes of superlattices in terms of simple properties of the elements that give rise to them, together with a series of experiments performed to test our conclusions. Evidence is presented that in some cases the process of ordering is more complex than might be supposed.

While the different species of atoms are usually found in random positions in alloy lattices, in some cases unlike atoms tend to be nearest neighbors. Bethe's[1] "order of neighbors" is a statistical measure of this tendency. At suitable compositions it is possible for atoms in large regions to be regularly arranged, which causes superlattice lines to appear in X-ray diffraction patterns. Bragg and Williams[2] have dealt with this "long-distance order" in their fundamental work on superlattices. Excellent discussions of superlattices are to be found in current reviews.[3,4]

Thermodynamic Considerations

Thermal vibration tends to destroy order. The magnitude of the effect can be determined from the entropy of mixing, which is calculated from first principles. Since the ordered state has the lower entropy, it must also have a lower internal energy to be stable at any temperature. The difference in internal energy determines the critical temperature at which long-distance order disappears. According to the theory of Bragg and Williams,[3]

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* Assistant Professor of Metallurgy, Graduate School of Engineering, Harvard University, Cambridge, Mass.

† Assistant Professor of Metallurgy, University of Kentucky, Lexington, Ky.

[1] References are at the end of the paper.

$$\Delta E = \tfrac{1}{2}RT_c$$

It may be assumed that differences in internal energy are largely due to interactions between nearest neighbors, since the crystal structure is otherwise practically the same. In considering the energy of interaction between the nearest neighbors in alloys of metals A and B, it will be found that only the quantity V is important.[5]

$$V_{ab} = \tfrac{1}{2}(E_{aa} + E_{bb}) - E_{ab}$$

where E_{aa} represents the *internal energy* due to interaction between a pair of A atoms which are nearest neighbors, etc., and V_{ab} represents the energy *given off* when a pair of nearest neighbors AB is formed. Positive V (attraction) favors miscibility, compound formation, and ordering. Negative V leads to immiscibility. Thermal agitation (the entropy term) works against both tendencies to form disordered solid solutions.

The value of V is influenced by the atomic size factor and by the chemical affinity of the atoms concerned.

When atoms of differing sizes are packed together in a close-packed arrangement, the lattice is distorted and local strains are set up. Large atoms are squeezed and small ones pulled apart. Both effects decrease V because the maximum attraction occurs only at the equilibrium distance. Superlattice structures are such that the strains are evenly distributed through the lattice and minimized.[7] Hence, difference in atomic size favors superlattice formation.

Attraction between atoms A and B makes V positive, which tends to increase the number of AB pairs, thereby favoring superlattice formation. Direct measurements are lacking, but attraction should lead to negative deviations from Vegard's law;[8] and tend toward the formation of stable compounds. In chemistry the most stable compounds occur between elements that differ greatly in electrochemical potential. Hume-Rothery[6] observes the same tendency in alloy systems. Pauling[9] finds in gaseous molecules that V increases with difference in electronegativity of the atoms concerned.

The conclusion may be stated that *ordered states should be found only where atoms differ considerably in size; or chemical nature; or both,* unless factors such as ferromagnetism play a part.

This conclusion is confirmed by experiment. Ordering is always found in alloys of gold, silver, or copper with the strongly electropositive alkali or alkaline earth metals, according to Dehlinger.[10] The list of 17 superlattices given by Barrett[4] shows that all except $FeNi_3$ and FeCo fulfill the above conditions. In these two, ferromagnetism perhaps plays a large part. However, the existence of the FeCo lattice is questioned by Hansen,[11] while Bradley and Taylor[12] could find no X-ray evidence for $FeNi_3$ using technique that succeeded with CuZn. It should be noted

here that AuNi, which is found in the list, has crept into the literature through a typographical error. The abstract of work by Westgren and Ekman[13] gives AuNi among alloys "not containing gold, silver, or copper." Obviously AlNi is meant.

Effect of Silver on the Gold-copper Superlattice

If the preceding argument is valid, it should be possible to predict various facts about the occurrence and stability of superlattices. In particular, it may be shown that silver substituted for a small part of the gold should lower the transformation temperature of the AuCu superlattice.

As can be seen in Fig. 1, the gold and copper atoms occupy alternate (001) layers in the face-centered AuCu superlattice. The *c* axis is slightly shorter than the other two, making the symmetry tetragonal. Each gold atom is surrounded by eight copper and four gold atoms, instead of six of each on the average, as would happen in a random distribution. Thus, in ordering, one-third of the Au-Au pairs are broken up to form Au-Cu pairs. It can be shown that for an alloy of N atoms, there are $\frac{1}{2}N$ Au-Au pairs and $\frac{1}{2}N$ Cu-Cu pairs broken to form N Au-Cu pairs. Hence, we have Q = atomic size factor + NV_{AuCu} for the energy of formation of the superlattice.

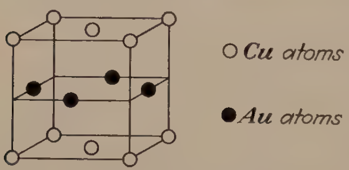

Fig. 1.—Unit cell of tetragonal gold-copper.

If a small percentage of silver, x, is substituted for a corresponding amount of gold, it will be found that $N(\frac{1}{2} - 2x + x^2)$ Au-Au pairs, $N(2x - 4x^2)$ Au-Ag pairs, $\frac{N}{2}$ Cu-Cu pairs, and $2x^2N$ Ag-Ag pairs are broken to form $N - 2xN$ Au-Cu pairs and $2xN$ Ag-Cu pairs, so that, neglecting x^2, Q' = atomic size factor + $N(1 - 2x)V_{AuCu} + 2xNV_{AgCu} - 2xNV_{AuAg}$.

Since the radius of silver is the same as that of gold within 0.2 per cent, the atomic size factors should be practically the same. Hence,

$$Q - Q' = 2xN\{V_{AuCu} - V_{AgCu} + V_{AuAg}\}$$

Gold and copper are completely miscible while silver and copper are nearly immiscible in the solid state. Since the size factors are the same in the two binary systems, this indicates that $V_{AuCu} - V_{AgCu}$ is positive. Furthermore, V_{AuAg} is no doubt positive, since gold and silver are completely miscible and have a negative deviation from Vegard's law. Hence, the energy of superlattice formation is decreased linearly by the substitution of silver for gold. This should decrease the critical temperature linearly, since $Q = \frac{1}{2}RT_c$.

We have carried out an extensive series of experiments, which verify this prediction.[14] In the course of the experiments, we have determined

several facts about the AuCu superlattice, which are perhaps not less important than the data we were seeking.

Experimental Work

The gold used for the preparation of alloys was purchased from the American Platinum Works and was stated to be 99.975 per cent pure. The silver was Mallinckrodt precipitated silver (analytical reagent) with the following maximum limits of impurities given on the label: chloride, 0.005 per cent; copper, 0.001; iron, 0.002; other heavy metals, 0.002; sulphate (SO_3), 0.05. The copper was high-purity electrolytic copper kindly supplied by the Raritan Copper Works.

The lattice constants of these metals, which give some indication of the purity, were found to be in good agreement with those given by Wyckoff[15] and by Jette and Foote[16] for metals of the highest purity obtainable, as follows:

Gold....................	4.0704 Å.; Jette and Foote give	4.0704 Å.
Silver....................	4.0783 Å.; Jette and Foote give	4.0779 Å.
Copper..................	3.6079 Å.; Wyckoff gives	3.6077 Å.

The silver was melted and coarse-filed to avoid mechanical loss of the fine powder; the gold and copper were also coarse-filed. All filings were treated with a magnet to remove possible contamination from the file. The three metals were weighed out in desired proportions into a Vitreosil tube of $\frac{3}{16}$-in. diameter, which was then evacuated and sealed off. The Vitreosil tube was lowered into a platinum-wound resistance furnace maintained at about 1200° C., and allowed to remain about five minutes. The tube was removed, broken open, and the ingot weighed. If the loss in weight was appreciable (more than 0.3 per cent), the ingot was rejected; otherwise, it was accepted without analysis. By this means, alloys were prepared containing 0, 1, 2, 3, 4 and 5 atomic per cent Ag substituted for a corresponding amount of gold in the 50 atomic per cent Au-Cu alloy. The 0 per cent Ag alloy had an excessive loss in weight (0.36 per cent), but analysis showed it to contain 50.0 per cent Au, so it was accepted.

The ingots, which weighed from 1 to 3 grams, were cold-worked and then annealed in a vacuum at 850° C. for 10 to 17 days in order to make them homogeneous. Filings from various parts of these samples gave sharp X-ray diffraction lines, proving them to be homogeneous.

After homogenizing, the ingots were reduced to filings by means of a fine file and portions of the filings were annealed. The annealing was carried out by sealing the samples in evacuated Pyrex glass tubes and lowering these tubes into a vertical tube furnace. The period of annealing extended from 2 hr. to 4 months, depending on the temperature of anneal, which varies from 250° to 600° C. Temperatures were held constant by Brown Instrument Co. controllers activated by chromel-

alumel or platinum-platinum rhodium thermocouples. Temperatures were frequently checked with a thermocouple that had been standardized against the melting point of pure zinc and of pure aluminum.

In order to secure uniform temperatures and a low-temperature gradient within the furnace, the following arrangement, described by Coffinberry and Hultgren,[17] was used. Through a vertical 1½-in. Vitreosil tube furnace, 12 in. long, were placed four Nichrome tubes $\frac{5}{16}$-in. inside diameter and 2 ft. long. The middle 4 in. of these tubes was surrounded by a solid cylinder of copper in which holes were made to accommodate the tubes. The control thermocouple was inserted in a hole in the block, but actual temperatures inside the Nichrome tubes were checked frequently by the standardized thermocouple. The copper block was nickel-plated for protection against oxidation. The temperature gradient was less than a degree for the middle inch, and 2° for the middle 3 inches.

For very accurate temperature control, which was desirable in some experiments, a precision temperature controller was constructed, after a design by Benedict.[18] The action of the controller is based on the change of resistance of a platinum resistance thermometer wound around the center portion of the copper core described above. This platinum wire is one arm of a resistance bridge, which is balanced at the proper temperature by a decade resistance box having 0.01-ohm steps. Any fluctuation in temperature unbalances the bridge and produces a very small current, which is fed through an amplifying circuit to the grid of an FG-57 Thyratron. The current flowing through the Thyratron is in series with the furnace winding and so regulates the temperature of the furnace. The precision of this control is said to be about 0.03° C. No variation in temperature of the furnace during a run could be detected on a Leeds and Northrup student potentiometer.

Upon completion of the anneal, the glass tubes containing the samples were expelled by ramming a steel rod through the Nichrome tube and were broken on an anvil under water. A very rapid quench was thereby obtained. After quenching, the samples were washed in alcohol, dried, and screened through a 100-mesh screen, which removed most of the broken glass. X-ray diffraction photographs were then made in a symmetrical back-reflection focusing camera. The line positions were measured and lattice parameters calculated by Cohen's analytical method.[19] It is estimated that results are correct to better than one part in ten thousand.

Results and Conclusions

The X-ray photographs of the thoroughly annealed samples were examined to identify the phases present and the lattice constants of these phases were determined as accurately as possible. The results are given

in Table 1. The phases found at various temperatures and compositions are plotted in Fig. 2. Results are most conveniently discussed under separate headings.

TABLE 1.—*Parameters of Alloys in One-phase Regions*
50 ATOMIC PER CENT COPPER; BALANCE GOLD AND SILVER

Atomic Per Cent Silver	Temperature of Anneal, Deg. C.	Days Annealed	a_0, Å.	c_0/a_0	Atomic Vol-ume, Å..	Structure
0	600	2	3.8669		57.82	F.C.C.
0	400	13	3.9484	0.9360	57.61	Ortho.
0	390	24	3.9515	0.9338	57.61	Ortho.
0	373	15	3.9510	0.9319	57.48	Tetr.
0	350	20	3.9512	0.9313	57.45	Tetr.
1	600	⅛	3.8676		57.85	F.C.C.
1	400	12	3.8669		57.82	F.C.C.
1	373	15	3.9518	0.9330	57.58	Ortho.
1	350	25	3.9504	0.9333	57.54	Tetr.
2	600	⅛	3.8669		57.82	F.C.C.
2	400	13	3.8667		57.81	F.C.C.
2	373	15	3.9459	0.9372	57.58	Ortho.
2	350	25	3.9551	0.9298	57.53	Ortho.
3	600	⅛	3.8683		57.88	F.C.C.
3	400	13	3.8682		57.88	F.C.C.
3	390	24	3.9450	0.9384	57.62	Ortho.
3	373	15	3.9507	0.9344	57.62	Ortho.
3	350	20	3.9562	0.9304	57.61	Ortho.
4	600	⅛	3.8674		57.84	F.C.C.
4	400	21	3.8674		57.84	F.C.C.
4	375	37	3.8668		57.82	F.C.C.
4	350	45	3.9420	0.9350	57.28[a]	Tetr.
5	600	⅛	3.8674		57.84	F.C.C.
5	400	21	3.8675		57.85	F.C.C.
5	360	23	3.8669		57.82	F.C.C.
5	350	45	3.9371	0.9360	57.12[a]	Tetr.

[a] Atomic volume low because of precipitation of gold-silver-rich phase.
F.C.C., face-centered-cubic disordered phase.
Ortho., orthorhombic ordered phase.
Tetr., tetragonal ordered phase.

Effect of Silver on Temperature of Ordering

As shown in Fig. 2, the substitution of silver for gold greatly lowers the temperature of ordering. Taking 420° C. as the best value of the critical temperature for the 0 per cent Ag alloy, 5 atomic per cent Ag lowers

the temperature by about 65°. With the exception of the 3 per cent alloy, the results are consistent. The first additions of silver have a greater effect than the later ones.

The Orthorhombic Phase

A very small, but sharp, splitting of certain of the tetragonal lines in the back-reflection X-ray pictures was observed in samples annealed just below the critical temperature. Such a splitting indicates that the b axis is no longer exactly the same length as the a axis. In addition, a number of new, weak lines appeared.

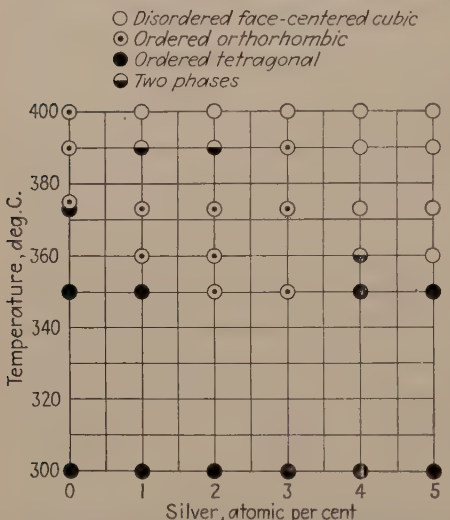

Fig. 2.—Phases present as function of temperature and percentage of silver.

Johansson and Linde[20] reported similar patterns in the AuCu superlattice two years ago. They found the structure to be orthorhombic, with the unit cell shown in Fig. 3. It is readily seen that the orthorhombic cell can be thought of as consisting of 10 tetragonal cells side by side, with gold and copper atoms reversing position after five cells. These units, however, are no longer exactly tetragonal; the b/a ratio differs slightly from one. We have assumed that our structure is the one reported by Johansson and Linde. They state that at 50 atomic per cent Au-Cu the orthorhombic phase can be obtained only by quenching from temperatures near 420° C. We find, however, that it exists over a wide tempera-

Fig. 3.—Unit cell of orthorhombic gold-copper.

ture range, nearly 50°. It seems not to be a metastable transition phase, since it can be obtained for the reaction proceeding in either direction; that is, from face-centered-cubic samples or from tetragonal samples, annealed at the same temperature. Furthermore, it persists after very long periods of anneal.

For simplicity, the centers of the split of the tetragonal lines were measured and the size of the pseudotetragonal cell, which is one-tenth of

the true cell, was calculated. According to Johansson and Linde, b/a for this cell is about 1.003. We have found it to vary in different samples. The larger values of b/a are found for samples annealed at lower temperatures, as shown in Table 2.

TABLE 2.—*Orthorhombic Splitting at Various Temperatures for* 50 *Atomic Per Cent Gold-copper Samples*

Temperature of Anneal, Deg. C.	Days Annealed	b/a	b/a after Six Months at Room Temperature
400	13	1.0018	1.0031
390	24	1.0017	1.0026
375	37	1.0025	1.0027

A most remarkable fact about the orthorhombic phase is its behavior at room temperature, where the tetragonal phase is presumably stable. After six months at room temperature, the small splitting of the tetragonal lines, which indicates that the structure is orthorhombic, becomes much greater; in some cases it practically doubles (Table 2). The change is thus not toward becoming tetragonal, which would be expected, but in the opposite direction. Samples in which the b/a ratio was originally large (annealed at temperatures near the lower limit of the orthorhombic phase) showed little increase in the splitting of the lines. There is no doubt as to the reality of the phenomenon; the lines are very sharp, and we have checked it in half a dozen cases. A tetragonal phase undergoes no perceptible change under the same conditions.

The Mechanism of Ordering

Bragg and Williams[2] picture ordering as a "continuous change of atomic arrangement within a single-phase system." The existence of an intermediate orthorhombic phase that does not pass gradually into the tetragonal phase stable at lower temperatures as the annealing temperature is decreased speaks against such a continuous change. Furthermore, there is some evidence of a two-phase region between order and disorder. Nix and Shockley[3] consider such regions theoretically inevitable but perhaps not realizable experimentally.

Various experimenters, beginning with Gorsky,[21] have reported X-ray pictures showing two phases present, simultaneously, one ordered and one disordered. All the samples were annealed for a comparatively short time of a few hours or a day. Since the reaction is known to be sluggish near the critical temperature, it is possible the two phases were not in equilibrium.

We have found two phases persisting even after 31 days of anneal with temperatures held constant within 0.5° C. The disordered phase had a definitely larger atomic volume in the two-phase region than it had when

quenched from a higher temperature, but the effect was small (0.2 per cent). This might be due to a change of composition such as would occur in a two-phase region. We do not consider the results conclusive, however.*

Lattice Parameters

Table 1 shows that the lattice parameter of the cubic phase decreases slightly just above the critical temperature. This is to be attributed to local order. Axial ratios of the superlattice decrease with the temperature of anneal, indicating that order is growing more perfect. Also, as order increases, the atomic volume decreases. The tetragonal cell has a smaller atomic volume than the orthorhombic.

Time for Equilibrium

The time necessary to attain equilibrium seems to be longer than many experimenters have realized. After 20 days at 350° C., the X-ray lines were still broad; 25 more days made them sharp. Since the time to attain equilibrium is an exponential function of the temperature, complete equilibrium can hardly be attained at temperatures much lower than this. Sixty-four days at 300° C. gave broad X-ray lines as expected. One hundred and twenty-seven days at 250° C. gave lines that could readily be measured, but they were not sharp. The experimenters who carried out relatively short anneals at low temperatures could not have attained equilibrium.

Summary

The argument is presented that the chief cause of superlattice formation is attraction between unlike atoms and differences in atomic size. Each of these causes has previously been recognized, but their simultaneous action has not been considered. Superlattices of which the existence has been established are composed of atoms differing considerably in size or electrochemical potential. Ferromagnetism may be an additional factor.

Thermodynamic reasoning indicates that silver substituted for gold in AuCu should lower the critical temperature of ordering. Experiments verify this prediction.

The orthorhombic, pseudotetragonal phase discovered by Johansson and Linde is found to be stable over a wider range of temperature than they had supposed. At lower temperatures, the well-known tetragonal cell is found. The pseudotetragonal cell of the orthorhombic phase has a b/a ratio very slightly greater than one. As the temperature of anneal decreases, toward the region of stability of the tetragonal phase, the

* Further experimental work on the FePd superlattice indicates that the ordering process is sufficiently sluggish to account for the simultaneous existence of two phases.

b/a ratio increases. Apparently, the transformation from orthorhombic to tetragonal does not take place gradually. At room temperature, the b/a ratio surprisingly increases with time.

The existence of the orthorhombic phase shows that the mechanism of ordering is not as simple as has been supposed. Some evidence is presented that there may be a two-phase region between order and disorder.

There is a small decrease in atomic volume just above the transformation temperature, attributed to order of neighbors in the absence of long-distance order.

At low temperatures the time necessary to attain equilibrium is longer than has been generally supposed.

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DISCUSSION

(E. E. Schumacher presiding)

E. E. Schumacher,* New York, N. Y. (written discussion).—After reading this interesting paper, it might be well perhaps to remind ourselves that the subject of superlattice formation is not of merely theoretical and academic interest. With this point in view, a few words concerning an event that occurred recently in a large manufacturing plant abroad during the fabrication of some wire might not be amiss. The composition of the alloy is, unfortunately, unknown to me. The annealing

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* Bell Telephone Laboratories.

practice normally used, and which had given satisfactory results for several years, consisted of heating the coils of heavy-gauge wire for several hours in a furnace and then pulling them out onto the floor to cool. On a recent occasion some delay at the end of the week prevented the floor-cooling of one lot of wire after the customary short anneal and the coils were left to cool with the furnace over the week end. The following Monday morning the wire coils were pulled from the furnace and dropped, as usual, a few feet to the floor. They broke into fragments. It was later definitely established that the brittleness of the wire resulted from superlattice formation.

Many of us have noticed anomalies in the behavior of certain alloys following heat-treatment. In some, superlattice formation, no doubt, has been involved in these anomalous behaviors. At any rate, very slow cooling, conducive to superlattice formation, results in brittleness in some instances. It is probably good practice, with alloys in which superlattice formation is known to be possible, not to prolong annealing times beyond the point where the desired softness is attained.

Tarnish Films on Copper

By J. B. Dyess* and H. A. Miley*

(Detroit Meeting, October, 1938)

Tarnish films on some of the common metals (particularly on copper and silver) have been of much scientific and commercial concern for a long time, but before the development of the electrical method[1] of measuring film thicknesses there was no satisfactory quantitative approach by which to study the separate parts of these complex films. This method has been adapted to the measurement of duplex (cuprous-cupric) oxide films on copper.[2] In the present work it has been used to measure tarnish films on copper when they were mixtures of cuprous oxide and cuprous sulphide, and also when they contained cuprous oxide, cupric oxide and cuprous sulphide, each component part being measured at a different potential value. Oxide-coated copper specimens, prepared by heating copper in air at chosen temperatures for given periods, were exposed to moist hydrogen sulphide in air to form the various oxide-sulphide films studied. The comparative resistances afforded by (1) different thicknesses of oxide films, and also (2) equal thicknesses of oxide and sulphide films, against severe attacks of hydrogen sulphide were measured.

The electrical method requires that the time be observed for the cathodic reduction of each part of the film substance, and these respective time values multiplied by the constant current give the corresponding quantities of electricity expended. Then each millicoulomb per square centimeter represents a film thickness of

$$t = \frac{M \times 10^8}{2D \times 96{,}494 \times 10^3} \qquad (a)$$

where M is weight of oxide (or sulphide) giving one gram-atom of oxygen (or sulphur) for cathodic reduction, D is density of the oxide (or sulphide) and t is the thickness in Ångström units per millicoulomb per square centimeter. The value of t for cuprous sulphide (cubical) is 14.27, and is obtained by substituting 5.78 for D and 159.20 for M in equation a. Previous values[2] of t for cuprous and cupric oxides (12.36 and 6.39, respectively) were used in the present work.

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* Physics Laboratory, Oklahoma Agricultural and Mechanical College, Stillwater, Okla.

[1] References are at the end of the paper.

Procedure

Sheets of copper No. 1, a good grade of commercial copper obtained from the Central Scientific Co., and copper No. 2, containing oxygen 0.04, sulphur, 0.003, and other impurities 0.007 per cent, which had been rolled to a thickness of 0.5 mm., were abraded with flint paper No. 0, cut into strips measuring 1.75 by 5.5 cm., washed in benzene, and rubbed dry with chemically pure cotton wool. Specimens not used immediately were kept in a desiccator over calcium chloride. The general agreement

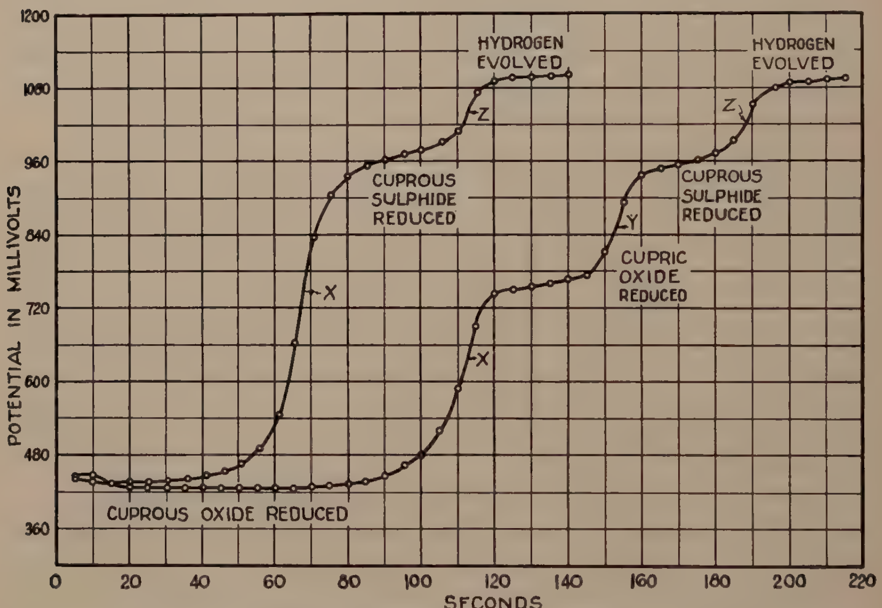

Fig. 1.—Potential-time curves.

Curve I is for a cuprous oxide-sulphide film on copper; curve II, for a triplex (cuprous oxide, cupric oxide and cuprous sulphide) film on copper.

between the values given by the two copper materials was good. The results discussed in this paper are for copper No. 1.

Equal areas of about 2.0 to 2.5 sq. cm. were selected at opposite ends of each specimen, and the rest of the specimen was covered with paint containing titanium dioxide dispersed in its weight of clear lacquer. A thickness measurement from one area of each specimen was recorded as a standard of comparison, and the thickness value of the other end was measured after exposure to hydrogen sulphide gas. The difference between the two thickness values provided a measure of the sulphide formed in the film.

In order to produce the sulphide components of the films, an open cardboard box containing the specimens was mounted on a porcelain

rack in a large desiccator, over water saturated with hydrogen sulphide gas. The concentration of the hydrogen sulphide was varied, when desired, by changing the amount of the saturated solution added to a given volume of water. Sufficient time was allowed to elapse after the desiccator was charged with the solution to allow equilibrium to be established before the specimens were introduced. All experiments of this nature were carried out at room temperature. The oxidation experiments, in an electric furnace at temperatures ranging from 220° to 270° C., were similar to those already described.[2]

The thickness values were obtained by subjecting the measured area to cathodic reduction in 0.1 M ammonium chloride solution at a constant current of 1.0 to 0.5 ma. per sq. cm., obtained by applying 220 volts through a resistance of 100,000 to 200,000 ohms. Potential-time curves have been obtained by noting the movement of the potential drop needed to force such a current through the cell: film-covered copper/ammonium chloride/copper. Typical potential-time curves* are given in Fig. 1. The inflection points X, Y and Z are considered to represent the instants when the respective cathodic reductions are completed, and these intervals are used in calculating the corresponding component thicknesses.†

Results

Thickness and Color.—Table 1 shows that the thicknesses of tinted films produced on copper by treatment with hydrogen sulphide gas at ordinary temperatures agree well with thickness values given[3] for oxide films of similar colors.

In the preparation of the sulphide films on copper, it was impossible, under the conditions of the experiment, to eliminate all of the cuprous oxide formed during and subsequent to the abrasion process. Specimens exposed to air for one day after abrasion gave an average thickness value of 80 Å. of cuprous oxide, which is in good agreement with the value given previously[3] for this film. Usually about 10 to 20 Å. of this initial oxide was replaced by sulphide during the hydrogen sulphide treatment. The numbers in column 2 include a mean value of about 65 Å. of the initial oxide.

A comparison of the total thickness values given in column 5, Table 2, with the values for corresponding tints given in column 3, Table 1, shows that uniformly tinted films of equal thicknesses produce similar colors whether they consist of one, two, or three component parts.

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* Potential-time curves for cuprous oxide films and cuprous-cupric oxide films have been given previously.[2]

† The word "thickness" refers to the depth that the film substance would have if it were spread uniformly over the area measured on the general plane.

As stated elsewhere,[2] this phenomenon indicates that the film consists of an intimate mixture of the film substances, and that the light is reflected mainly from the outer and inner surfaces of the film.

TABLE 1.—*Thickness of Sulphide and Oxide Films on Copper*[a]

Tinted to	Thickness of Film, Å.	
	Sulphide	Oxide
First order:		
Dark brown	340	370
Red brown	390	410
Purple	440	460
Violet	470	485
Blue	510	520
Silvery green	815	800
Second order:		
Yellow	970	940
Orange	1,100	1,170
Red	1,230	1,240
Purple violet	1,450	
Blue	1,540	

[a] Values given in the second column are mean values obtained from a large number of experiments recorded during the period of this research. Values given in succeeding tables of this paper are single values, representative of the respective types of experiments described.

TABLE 2.—*Thickness of Duplex and Triplex Films on Copper*

1	Thickness of Film, Å.			
Tinted to	2 Cu_2O	3 CuO	4 Cu_2S	5 Total
First order:				
Light brown	94		185	279
Purple	230		225	455
Dark violet	218		295	513
Second order:				
Greenish yellow	618	36	316	970
Red	955	45	232	1,232

Formation and Composition.—Numerous properties of sulphide films on copper have been studied by Evans,[4] Vernon,[5] and Constable.[6] A number of the observations of these researches have been confirmed in the present work. The rate of growth of the sulphide film under the conditions of the present experiments increased with the concentration of the

hydrogen sulphide gas. The presence of moisture* in the atmosphere or on the specimen enhanced the rate of formation of the sulphide.

No evidence was obtained of the formation of any sulphide other than cuprous sulphide, and it is considered that the cubical form of this sulphide is the one formed.[7]

Vernon observed that specimens exposed to a tarnishing atmosphere often produced later colors at the edges and earlier ones toward the centers. Evans showed, by experiments in closed vessels, that such edge effects occurred only when the concentration of hydrogen sulphide was very small, and attributed it to the greater replenishment of the attacking gas at the edges.[8] In agreement with Evans' explanation, the authors have found that the edging effect can be greatly reduced by surrounding a specimen with strips of copper placed in physical contact with it.

When oxide-coated specimens were exposed to moist hydrogen sulphide gas, some of the oxygen, from both cuprous and cupric oxides, was replaced by sulphur. Specimens containing oxide films of thicknesses given in column 1 of Table 3 were exposed simultaneously for 3 min. to moist hydrogen sulphide gas. Column 2 represents the amount of the oxides remaining in the film after this treatment, column 3 that of the sulphide formed and column 4 that of the oxides replaced. The total amount of the sulphide formed and of the oxides replaced was increased in other experiments by increasing the time of exposure to the hydrogen sulphide attack.

TABLE 3.—*Replacement of Oxide by Sulphide in Copper Oxide Films*

1		2		3	4	
Initial Oxide, Å.		Residual Oxide, A.		Sulphide Formed, Å.	Replaced Oxide, Å.	
Cu_2O	CuO	Cu_2O	CuO		Cu_2O	CuO
116		102		206	14	
193		164		159	29	
528		383		378	145	
1,598	100	1,463	76	253	135	24
1,902	183	1,665	114	339	237	69

Conditions were chosen so that pairs of specimens exposed simultaneously to hydrogen sulphide yielded thickness measurements in such good agreement as to allow them to be considered identical. One of each pair was measured as a standard of comparison, and the second specimen of each pair was heated in an electric furnace for a given period.

* Evans found[4] that when the concentration of hydrogen sulphide was very small (much smaller than that used in the present experiments) the rate of growth was retarded by increases in the moisture.

Then the thickness measurement of the second specimen was compared with that of the first to ascertain whether any sulphide had been replaced by oxide. Table 4 gives the results of four such experiments.

TABLE 4.—*Comparison of Sulphide Amounts in Films before and after Heat-treatment*

Specimen No.	1 Before Heating, Å.		2 After Heating, Å.		3 Changes, Å.	
	Cu_2O	Cu_2S	Cu_2O	Cu_2S	Cu_2O	Cu_2S
1	89	146	298	154	209	+ 8
2	94	85	173	103	79	+18
3	100	91	163	86	63	− 5
4	111	63	160	85	49	+22

There was no apparent loss in sulphide, even after relatively long heat-treatments. Small negative values, such as that shown in the sulphide part of column 3, are attributed to failure to obtain identical films of sulphide in such pairs of specimens. An average of a large number of the apparent changes indicated that a small increase of approximately 10 Å. occurred in the sulphide amount. This increase is attributed to small amounts of absorbed hydrogen sulphide, which had not reacted before the heat-treatment.

Protective Quality.—The protective quality of oxide films of various thicknesses was studied by exposing these films to hydrogen sulphide simultaneously and determining the amount of cuprous sulphide formed. The amount of sulphide reacting with the copper, and the amount of sulphur replacing oxygen in the oxide layer of the film varied with the protective quality of the film and with the reaction time.

Curve II of Fig. 2 shows clearly the protection afforded by oxide films against attacks by hydrogen sulphide. Curve II represents the total sulphide formed, consisting of: (1) the amounts resulting from the diffusion through the oxide film, and (2) the amounts produced by the replacement of oxide. Curve I represents only the first of these amounts. Thin films containing pores and thick ones that are cracked give less protection than those of the intermediate thickness range, approximately 125 to 275 Å. The pores decrease with increase of thickness until the most continuous film and the one of maximum protection is obtained at approximately 200 Å. The increasing pent-up stresses owing to the fact that the volume of the film is greater than that of the metal used cause minute cracks to appear in the film when its thickness approaches the upper end of the range of intermediate thicknesses. As the film thickens further, it becomes increasingly more difficult for the reactants to penetrate the oxide layer, and it appears that an appreciable time is

required for the reaction to start. When the period of exposure is increased sufficiently, relatively large quantities of sulphide are produced in the oxide films of greater thicknesses, as shown by curve III of Fig. 2. These observations concerning the protections afforded by oxide films of various thicknesses are in good agreement with the results of Evans' well-known experiment with silver nitrate drops.[9]

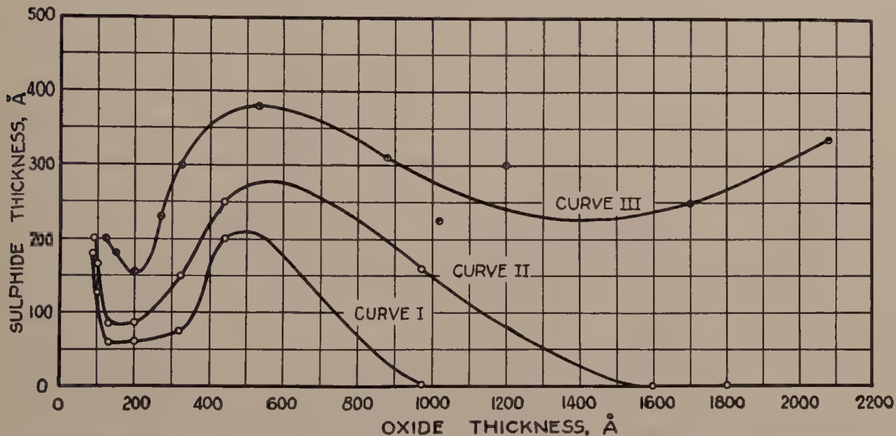

FIG. 2.—SULPHIDE FORMED BY EXPOSING OXIDE-COATED COPPER TO MOIST HYDROGEN SULPHIDE IN AIR.

Curve I represents the amounts of sulphide formed by direct reaction between the hydrogen sulphide and the base metal during an exposure of 80 sec. Curve II shows the total amounts of sulphide formed in the 80 sec. (the amounts represented by curve I and those produced by replacing some of the oxide). Curve III represents the total sulphide formed on a different series of specimens when exposed for 180 seconds.

Specimens containing oxide and sulphide films of several thicknesses were exposed simultaneously to moist hydrogen sulphide gas for 3 min. Representative results are given in Table 5, showing that larger quantities of sulphide were added to the oxide films. Under the conditions

TABLE 5.—*Comparison of Sulphide Formed in Oxide and Sulphide[a] Films*

Initial Thickness of Films, Å.			Thickness of Films after Exposure to H_2S, Å.				Change in Thickness, Å.			
Film I		Film II	Film I		Film II		Film I		Film II	
Cu_2O	Cu_2S	Cu_2O	Cu_2O	Cu_2S	Cu_2O	Cu_2S	Cu_2O	Cu_2S	Cu_2O	Cu_2S
57	93	140	56	220	94	185	1	127	46	185
56	246	315	53	360	218	295	3	114	97	295
57	392	528	57	525	383	368	0	133	145	368
44	1,190	1,194	44	1,352	1,188	300	0	162	6	300

[a] The sulphide films contained the nonreplaced part of the ordinary air-formed oxide film.

of these experiments,* it appears that oxide films afford less protection against hydrogen sulphide attacks than sulphide ones of similar thicknesses. A possible explanation of this difference in protective qualities is given in the theoretical considerations.

Theoretical Considerations

After studying these results and those of previous workers, the authors are giving some of their views concerning the mechanism of the tarnishing of copper in a moist atmosphere containing hydrogen sulphide gas. Any future change or modification in these views, influenced by new or extended researches, should not affect the experimental results recorded above.

The following equations are considered to represent the expected reactions when copper, containing some cuprous oxide, is exposed to moist hydrogen sulphide in air:

$$2Cu^+ + 2H^+ + S^= \rightarrow Cu_2S + 2H^+ \qquad [1]$$

$$2H^+ + O^= \rightarrow H_2O \qquad [2]$$

$$\left.\begin{array}{l} 2H^+ + 2Cu^+ + O^= \rightarrow H_2O + 2Cu^+ \\ 2Cu^+ + 2H^+ + S^= \rightarrow Cu_2S + 2H^+ \end{array}\right\} \text{Effect on cuprous oxide} \qquad \begin{array}{r} [3a] \\ [3b] \end{array}$$

Equations 1 and 2 involve: (*a*) the ionization of hydrogen sulphide in the moisture layer on the outer surface of the film, (*b*) the diffusion of copper cations and electrons from the base metal outward across the film and sulphur anions inward, and (*c*) the possible reaction of the hydrogen ions with any accessible oxygen from the air that becomes ionized. When the film contains some cuprous oxide, the reactions represented by equations 3*a* and 3*b* may proceed one or more times before the same amount of hydrogen ions combine with oxygen from the air according to equation 2. Price[10] has reviewed recent German advances in the mechanism of oxidation and tarnishing of metals, and has given much evidence in support of C. Wagner's theories,[11] which postulate the diffusion of cations and electrons outward and anions inward through the film. The diffusion of either the cations or anions is usually negligible and it is possibly the large anion that diffuses least in the present experiments.

It appears now that all of the observations can be explained:

1. An increase in the concentration of the hydrogen sulphide gas increases the rate of supply of sulphur ions and hence the rate of formation of sulphide.

2. When the hydrogen sulphide concentration is high, an increase of moisture increases the amount of the irregular surface that is covered with a moisture film (until the entire surface is covered). This increases

* These observations were made on severe attacks of hydrogen sulphide and should not be confused with results obtained from exposures to normal atmospheric conditions.

the area exposed to the attacking ions, thus increasing the rate at which sulphide is produced. If the concentration of the attacking gas is very small, a large amount of moisture will decrease the number of ions per unit volume in the moisture film. This reduced ionic concentration limits the number of ions reaching the reaction surface and accordingly decreases the rate of the sulphide formation.

3. Equation 1 is considered to represent the primary reaction because: (*a*) the total amount of sulphide added to the oxide films was generally much larger than the amount that could be accounted for by the replacement of oxide, and (*b*) when the film thickness became too great to permit the formation of sulphide in a given time by diffusion, no sulphide was formed by the replacement of oxide. After some ionized hydrogen is made available by the primary reaction, the amount of oxide replaced by the reactions represented by equations 3*a* and 3*b* depends on the accessibility of ionized oxygen and oxide. Rarely did the total amount of sulphide formed appear to approximate that accounted for by the replacement of oxide. In the absence of oxygen, oxide would be replaced, and after the replacement of the accessible oxide molecular hydrogen would probably be liberated.

4. Generally the rate of growth of a solid film on a metal surface is controlled by the rate of diffusion of the anions and cations, but the rate of growth may be controlled in some cases by the diffusion of the electrons through the film.[10] Since the specific resistance of cuprous sulphide is possibly greater than that of cuprous oxide, further experiments may show that the differences observed in the protective qualities of sulphide and oxide films (Table 5) are due largely to differences in the electrical conductivities of the film substances.

Summary

1. The electrical method of measuring film thickness was used to measure tarnish films on copper when they were mixtures of cuprous oxide, cupric oxide and cuprous sulphide.

2. Copper sulphide films are shown to have approximately the same thickness values as copper oxide films of the same colors and orders.

3. Mixtures of oxide and sulphide films giving uniform tints were found to have total thickness values consistent with the values for oxide films of similar colors.

4. Previous electrical measurements of the rapid formation of invisible oxide films at ordinary temperatures were confirmed.

5. When oxide-coated copper was exposed to moist hydrogen sulphide in air copper sulphide was formed: (1) by combining some sulphur with copper from the base metal, and (2) by replacing some oxygen from the oxides by sulphur.

6. No evidence was obtained of the replacement of sulphur by oxygen, even when the sulphide films were subjected to oxidation treatment in an electric furnace.

7. Thin oxide films containing pores and thick ones with cracks gave less protection against severe attacks of moist hydrogen sulphide in air than films of the intermediate thickness range. This range of greatest protection was found to be approximately 125 to 275 Å., the thickness giving maximum protection occurring at about 200 Å.

8. It was observed that sulphide films gave more protection against severe attacks of moist hydrogen sulphide in air than oxide films of equal thicknesses.

9. The authors gave some of their views concerning the mechanism of the tarnishing of copper by moist hydrogen sulphide in air.

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5. W. H. J. Vernon: *Trans.* Faraday Soc. (1923) **19**, 839; (1927) **23**, 117; *Jnl.* Chem. Soc. (1926) 2273.
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9. U. R. Evans: *Nature* (1926) **118**, 51. See also *Jnl.* Chem. Soc. (1925) 2491.
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11. C. Wagner: *Ztsch. physik. Chem.*, *B* (1933) **21**, 25; (1936) **32**, 447.

DISCUSSION

(*Ernest B. Drake presiding*)

L. E. Price,* Cambridge, England (written discussion).—The value of this method lies in the ease with which tarnish products can in certain cases be analyzed. In conjunction with Thomas,[12] I have been able to use the method for analyzing the tarnish products on silver and its alloys.

It does, however, seem desirable to compare the reduction potentials with those calculated from known data. It is therefore unfortunate that the potentials are not given against some standard electrode. In our own work we have compared the calculated values with those actually found and observed that the reduction potential of cuprous sulphide agreed fairly well with that calculated, but that the potentials for cuprous and cupric oxides were markedly more negative. On reducing the current density the potential for cuprous oxide approached the calculated value asymptotically.

It is very doubtful whether the estimation of cuprous sulphide is as accurate as suggested. The authors assume that the whole of the current is, in this case also,

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* University of Cambridge.

[12] L. E. Price and G. J. Thomas: *Jnl.* Inst. Metals (1938) **63**, 29.

utilized in the reduction of the sulphide, even though the potential is only 0.1 volt more positive than the potential for hydrogen evolution. It has been clearly established that the potential at which hydrogen is evolved is a function dependent upon the nature of the surface and the current density and the amount of hydrogen liberated at the cuprous sulphide potential may be by no means negligible. The estimation may therefore only be semiquantitative. This objection does not apply to the estimation of cuprous or cupric oxides.

Wagner[13] and Reinhold and Möhring[14] have shown, at least for cuprous oxide and cuprous selenide, which is almost certainly analogous to cuprous sulphide, that the anions in the lattice are immobile while the cations can diffuse fairly readily through the lattice. Modern theories of film growth thus readily explain the failure to convert copper sulphide into the oxide but provide no ready explanation for the mechanisms involved in the sulphidation of the oxide. It is difficult to see how equations 3*a* and 3*b* can apply to anything but the outermost layer of molecules.

W. H. J. Vernon,* Teddington, Middlesex, England (written discussion).—Congratulations are due to the authors for the ingenious way in which they have adapted Dr. Miley's electrical method to the study of complex sulphide and oxide films on copper. The differentiation which this permits between the several constituents is particularly striking and further applications will no doubt follow in due course. At the present stage, however, caution would seem to be necessary in the quantitative interpretation of results. Work recently completed at Teddington[15] on thin oxide films on iron, using chemical methods, supplemented by the vacuum fusion method of H. A. Sloman, has yielded film-thickness values considerably less than those previously reported by Dr. Miley.[16] It seems probable that the discrepancy may be associated with difficulties in fixing the position of the critical point on the potential-time curve (e.g., x,y,z in Fig. 1); other possible sources of error have been discussed elsewhere.[17] In Tables 2 and 3 film-thickness values are expressed to the nearest Ångstrom unit. It is hardly likely that the authors would wish to claim this degree of accuracy; the view reached at Teddington is that no method of film-thickness determination is capable of approaching such accuracy even if the demarcation between surface film and basis metal were sufficiently precise to demand it.

It is important to bear in mind (as stated by the authors in the footnote on p. 246) that the tarnish films described in the paper are all "synthetic" in character, and consequently their properties do not necessarily correspond with those formed under service conditions. In my First and Second Reports to the Atmospheric Corrosion Research Committee[18] (work conducted under auspices of British Non-ferrous Metals Research Association) it was shown that the properties of the two types of film are in certain respects very dissimilar. For example, in contrast with the present results, thin films of oxide on copper were found to be extremely protective towards ordinary indoor tarnishing, while initial films of sulphide of equivalent thickness actually promoted further oxidation. The authors' opening paragraph suggests that they

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13 C. Wagner: *Ztsch. phys. Chem.* (1933) **22-B,** 212; (1937) **37-B,** 155; (1938) **40-B,** 197.

14 H. Reinhold and H. Möhring: *Ztsch. angew. Chem.* (1935) **48,** 709.

* Chemical Research Laboratory, Department of Scientific and Industrial Research.

15 W. H. J. Vernon, F. Wormwell, T. J. Nurse: The Thickness of Air-formed Oxide Films on Iron. *Jnl.* Chem. Soc. (1939) 621.

16 *Carnegie Schol. Mem.*, Iron and Steel Inst. (1936) **25,** 197.

17 *Jnl.* Iron and Steel Inst. (1937) **135,** 409P, 412P.

18 *Trans.* Faraday Soc. (1923) **19,** 839; (1927) **23,** 113.

are unaware that the composite character of "natural" tarnish films (those formed by exposure to ordinary room atmosphere) had been established some time ago by chemical methods (Second Report, p. 123). On p. 243, my early observation concerning the "edge effects on specimens tarnishing in room atmospheres is referred to, but the "explanation," worked out in a whole series of experiments (First Report, p. 894 et seq.), is attributed elsewhere. Actually, the importance of the "diffusion factor," which operates characteristically on free exposure as distinct from exposure in closed vessels, was emphasized repeatedly in both the First and Second Reports. It was also shown in the First Report that tarnishing due to very small (atmospheric) concentrations of hydrogen sulphide is hindered by thin moisture films. The authors' technique, however, represents a great advance in this field, and further developments (particularly in the study of films produced in atmospheres containing much lower concentrations of hydrogen sulphide than those employed in the present work) will be warmly welcomed.

D. H. Bangham,* London, England (written discussion).—A striking feature of the results is the marked decrease in the porosity of the cuprous oxide films as their apparent thickness undergoes the proportionally very small increase from ca. 90 to 110 Å. This is evidenced by the rapidly falling sections of the curves of Fig. 3 near the ordinate axis, indicating a marked decrease in the rate of attack by hydrogen sulphide as the oxide film increases in thickness between these two limits. A further exploration of this region, though clearly difficult, might well throw some light on the structure of these very thin films. One possible explanation, which accords with some unpublished work of the present writer, is that film formation starts from nuclei, and that lateral growth takes place simultaneously with thickening.

J. B. Dyess and H. A. Miley (written discussion).—The authors are glad that Dr. Price and Dr. Thomas have been able to use the electrical method for analyzing the tarnish products on silver and its alloys. The silver-alloy products are more complicated, and it is clearly more difficult to assign the reduction potential values to the respective products than in the present investigation. The oxides had been measured previously, and the addition of the sulphide component provided only one additional reduction potential. Dr. Vernon stated that the composite character of the natural tarnish films had already been established; the authors wish to emphasize that their experiments were directed toward the measurement of the tarnish products on copper rather than toward their analysis.

The relative closeness of the potential values at which cuprous sulphide is reduced and hydrogen evolved was recognized by the authors. It is well known that when the thermodynamic conditions appear to be such as to permit two reactions to proceed simultaneously the primary one may repress the secondary one until it has been completed. In the present case, however, there is an appreciable difference between the potential values resulting in a well-defined and reasonably sharp transition between the reactions (Fig. 1,z). The consistency of the results, particularly the constancy of the color values obtained from mixed films, consisting of varying percentages of sulphide, lead the authors to believe the sulphide determinations sufficiently quantitative to justify the conclusions recorded. The thickness values shown in the tables beyond the first one are given to the nearest Ångstrom unit merely because they are single values and representative to the respective types of experiments, as was explained in the note following Table 1.

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* The British Coal Utilisation Research Association.

The authors suggested (p. 246) that the relatively large oxygen and sulphur anions diffuse less than the copper cations. Dr. Price's reference to Wagner's work as showing that the oxygen anions and possibly the sulphur are immobile, while the cations can diffuse fairly readily through the lattice, offers an explanation not only for the failure to convert copper sulphide into the oxide but also for the replacement of some of the oxide by the sulphide. Assuming that the oxygen and sulphur anions are immobile, equation 1 involves the outward migration of the copper cations and electrons from the base metal followed by the inward migration of the hydrogen cations liberated from this reaction. The hydrogen ions may migrate to appreciable depths within the film or remain near the surface until they combine with oxygen anions as represented by equation 2 or 3*a*, depending on the accessibility of the respective anion sources. If the reaction proceeds as shown in equation 3*a*, the freed copper cations migrate to the surface to react as shown in equation 3*b*. It should be emphasized that equations 1 and 3*b* may be identical surface reactions, the cations of the first being supplied from the base metal while those of the latter are released from the oxide film. In neither case is it necessary to consider that the anions penetrate the film.

The results for oxide films on iron (ref. 1 of Dr. Vernon's discussion) will be awaited with much interest. Caution should be exercised before assuming that the results of any single method are correct and that quantitative interpretations of different measurements obtained from another method may not be correct. The methods may be measuring different things; the large discrepancy between the gravimetric results of Dr. Vernon and others and the optical results of Constable and others was explained on this basis (Dr. Vernon's ref. 2) without assuming that there were any inaccuracies in the different sets of measurements. Dr. Vernon raised a question concerning the accuracy of the value of the index of refraction employed by Constable (Dr. Vernon's ref. 3); Leberknight and Lustman[19] have recently obtained, by a very different method, an average value for the index of refraction of oxide films on iron, which is very close to Constable's value. Their method may accordingly yield thickness values in good agreement with those given by the electrical method.

The difference between the films formed from severe attacks of hydrogen sulphide and those formed under service conditions was emphasized by the authors (footnote, p. 246). Because of this difference, they made no attempt to correlate the two sets of results on protective quality. In the authors' experiments the electrical conductivities of the film substances may have determined the protective qualities while in the less severe attacks of service conditions the diffusion of the cations may have determined the protection afforded.

The authors devoted only three sentences to the "edge effect" observed by different workers. Reference 8 was selected because it directs the reader to a concise explanation based on both experimental observation and mathematical consideration and to the work of Dr. Vernon and also that of L. R. Luce. In referring to his own work[20] Dr. Vernon stated, among other things, that " . . . the tarnishing of copper under ordinary conditions *appeared* to be favored by a low relative humidity and hindered when the concentration of water vapour was excessively high." In the same introductory discussion he referred to the work which he considers to be confirmatory and said, "It has since been shown by U. R. Evans that if the concentration of hydrogen sulphide is sufficiently low, tarnishing is actually hindered by the presence of a film of moisture on the metal surface." The authors have no desire to attribute incorrectly any of the conclusions of others; in order not to occupy too much space, very little has been devoted to the discussion of the work of others, but if the references

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[19] C. E. Leberknight and B. Lustman: *Jnl.* Optical Soc. Amer. (1939) **29,** 63.

[20] W. H. J. Vernon: *Trans.* Faraday Soc. (1927) **23,** 117.

are followed the observations and conclusions of Dr. Vernon, and those of Constable, Evans and others will be brought before the reader.

The Central Scientific Co. has recently given to the authors information showing that the copper No. 1 mentioned in the paper was 99.99 per cent pure.

Dr. Bangham's suggestion that film formation may start from nuclei and lateral growth proceed simultaneously with thickening is interesting. The term "pores" may refer largely to discontinuities in the earliest film formation and to the relatively thin places in later ones.

Electron Diffraction Effects from Polished Zinc Surfaces

By M. L. Fuller,* Member A.I.M.E.

(Detroit Meeting, October, 1938)

During the last several years many papers have appeared dealing with the structure of highly polished metal surfaces. The awakening of interest in this subject is due to the applicability of the electron diffraction technique to the study of surfaces. The original theory of Beilby[1] considered the surface of polished metals as of the nature of a supercooled liquid or a vitreous, amorphous solid. The electron diffraction effects from polished metals have been interpreted by many to be a direct experimental proof of the correctness of the Beilby theory. This interpretation has been strongly opposed by others, so that at the present time the subject is in an uncertain and controversial state.

In the present paper new, and hitherto unpublished, electron diffraction effects from polished zinc are described. These observations indicate that the polished surface of zinc is crystalline.

Published Work

Many papers[2–10] have interpreted the electron diffraction evidence as proof of the Beilby amorphous theory. All investigators agree that highly polished metals give rise to two diffuse diffraction haloes, similar to those obtained by the diffraction of X-rays in liquids and vitreous solids. It is this similarity that leads to the amorphous-layer interpretation of polished metals. Strangely, the interatomic distances calculated from these haloes are very similar for the various metals investigated, in spite of a rather wide range of such distances in the crystalline and liquid states. The calculated atomic sizes are, furthermore, smaller than are experienced in the normal states of the metals. In spite of these anomalies, the amorphous-layer interpretation has been adhered to by many. One investigator, S. Dobinski,[11] differs from the others in his experimental results. By polishing under benzene in order to avoid the possibility of oxidation, Dobinski obtains diffuse haloes of radii different from those previously obtained. He thus obtains a more rational quantitative correlation of the diffuse haloes with the amorphous-layer theory.

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* Investigator, Metal Section, Research Division, The New Jersey Zinc Co., Palmerton, Pa.

[1] References are at the end of the paper.

On the other hand, L. H. Germer[12] and F. Kirchner[13] have produced evidence showing that the diffuse haloes are obtainable from materials that are definitely crystalline. For example, Germer has obtained two diffuse haloes by the reflection of electrons from a thin film of evaporated zinc sulphide condensed on a glass plate. The same film, flaked away from the glass and examined by the transmission of electrons, yielded a normal Debye-Scherrer diffraction pattern typical of crystalline zinc sulphide. Kirchner has performed a similar experiment with gold leaf. Further experimental work in Kirchner's laboratory[14,15] has led him to the conclusion that whether one obtains the diffuse haloes or a typical crystalline pattern depends on the "Rauhigkeit" of the surface, which may be interpreted as the "surface texture." It is generally recognized that the diffraction patterns obtained by the "reflection" of electrons are really due to the transmission of the electrons through ultramicroscopic projections at the surface of the specimen. When the surface becomes extremely smooth and the projections extremely small, as in polishing, the available grating area of each projection will be too small for efficient diffraction, resulting in a diffusion of the lines of the pattern. Refraction of rays entering and leaving the same crystal surface may also affect the appearance of the diffraction maxima.

G. I. Finch, one of the most active supporters of the amorphous interpretation, now admits[16] that the evidence for the diffuse halo "can only be regarded as such as to leave in doubt the issue as to whether the polish layer is crystalline or amorphous." Finch continues to hold to the amorphous theory, however, on the basis of other, indirect evidence. This indirect evidence is based on the experimental observation that polished metal surfaces have the ability to dissolve other metals, deposited thereon by sputtering, much more rapidly than do ordinary metal surfaces. It seems probable, however, that a polished surface, consisting of extremely fine crystals, could equally well account for this high diffusion rate. The extremely fine crystals would present an unusually high crystal surface and would thus be very amenable to rapid diffusion.

The Camera

The electron diffraction camera is of the hot-filament type. In the design of the camera the writer was greatly assisted by the privilege of inspecting two other electron diffraction units. The courtesy and advice of Dr. L. H. Germer, of The Bell Telephone Laboratories in New York, and of Dr. Raymond Morgan, of the Randall-Morgan Laboratory of Physics, University of Pennsylvania, in this regard, are deeply appreciated. The cathode assembly, anode, and slit system are patterned closely after Germer's camera.[17] The plate-holder end of the camera is very similar to that of Morgan and Smith.[18] The fluorescent screen is

made with specially prepared willemite supplied through the courtesy of Dr. H. W. Leverenz,[19] of the R. C. A. Laboratories.

The specimen-holding device is designed especially for the study of surfaces by the reflection of electrons. Manipulation of the specimen is carried out by means of Sylphon corrugated copper bellows. Thus the specimen may be independently adjusted in angle with the incident electron beam or moved in or out of its path. Provision is also made for varying the position at which the beam strikes the specimen and for bringing several specimens successively into the path of the beam.

In using the camera for this investigation, the following conditions were employed:

Electron voltage, 40 to 45 kv., actual voltage for each photogram being determined by recording a reference pattern.

Grazing angle of incidence of electron beam on specimen approximately 0.5°.

Distance from specimen to photographic plate, 38.1 cm.

Electron Diffraction Observations on Polished Zinc

A large number of polished zinc surfaces were examined in the electron diffraction camera. It was discovered that polished zinc gave rise in some instances to diffraction effects in addition to the two diffuse haloes reported in the literature.

Fig. 1 is a reproduction of the several typical photograms upon which this paper is based. *A* shows the two diffuse haloes generally obtained from polished metal surfaces. This specimen was produced by careful metallographic polishing, such as is used in the preparation of specimens for metallographic examination. The polishing was carried out according to methods developed by J. L. Rodda,[20] of this laboratory. Carefully prepared abrasives were employed in such a manner as to produce a minimum of distortion of the underlying grain structure. The excellence of this polishing technique in producing a high optical polish with very little distortion has been demonstrated in these electron diffraction studies. Many of the specimens did not yield the halo type of diffraction pattern typified by photogram *A* but yielded a diffused pattern of crystalline zinc. The diffuse-halo pattern, *A*, was obtained with about equal frequency, with no apparent change in polishing technique. In rare cases the pattern of photogram *B* is obtained by the same polishing procedure. Photogram *B* is a definite indication of crystallinity. Diffraction lines perpendicular to the shadow edge intersect the haloes, yielding a pattern analogous to those obtained from single crystals or highly oriented polycrystalline surfaces.[23,24]

Photograms *D*, *E* and *F* show similar diffraction effects, those of *D* being barely perceptible and those of *E* and *F* being strongly developed. The latter group of photograms was obtained with polished specimens

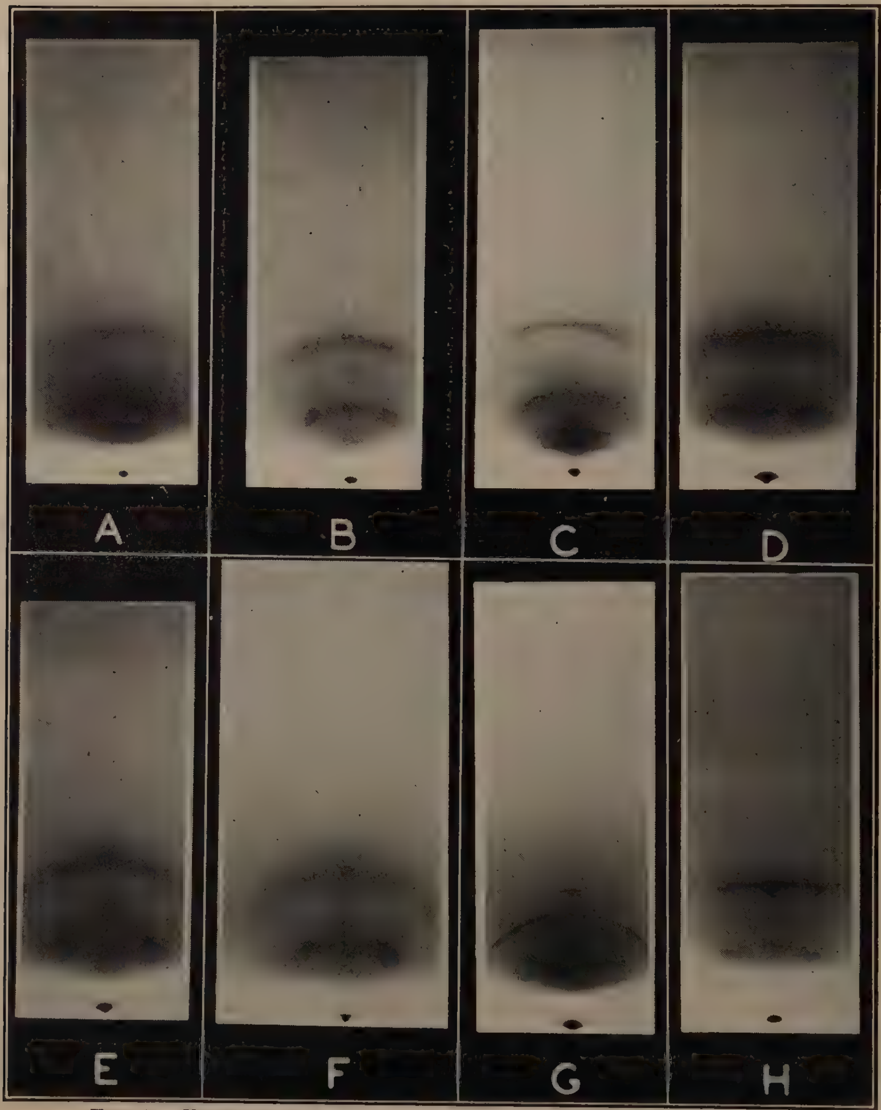

FIG. 1.—ELECTRON DIFFRACTION PHOTOGRAMS FROM POLISHED ZINC.[a]

PHOTOGRAM	TREATMENT OF SPECIMEN	DIFFRACTION EFFECTS
A	Zinc, metallographically polished	Two haloes
B	Zinc-base alloy,[b] metallographically polished	Two haloes, three vertical lines
C	Identical with *A*, but small angle of incidence of electron beam.	Three haloes
D	Zinc, metallographically polished, annealed 16 hr. at 50° C.	Two haloes, faint intensity maxima at points of intersection of vertical maxima
E	Zinc, metallographically polished, annealed 50 hr. at 50° C.	Two haloes, three vertical lines
F	Zinc, metallographically polished, annealed 18 hr. at 50° C.	Two haloes, five vertical lines
G	Zinc, buffed with commercial buffing compound	Spots produced by intersecting horizontal and vertical maxima and polycrystalline zinc oxide rings
H	Zinc-base alloy,[b] buffed with commercial buffing compound	Four horizontal lines with spots produced by intersecting vertical lines

(For remainder of legend see opposite page)

which had been annealed at 50° C. These specimens gave the diffuse-halo pattern *A* before annealing and developed the vertical diffraction maxima as a result of the annealing.

It may be hypothesized that these data indicate that as the zinc is polished the crystals become broken up into smaller and smaller units, resulting in a diffusion of the normal polycrystalline type of diffraction pattern. Plastic deformation takes place at the same time, which results in a reorientation of the crystals by the well-known slip-rotation process whereby the crystals align themselves with the slip plane (basal plane of the hexagonal close-packed zinc structure) parallel to the surface of polish. The oriented crystalline structure type of pattern was developed by polishing only in the specimen of photogram *B*, but annealing was required for photograms *E* and *F*. It is suggested, in regard to the specimens typified by photogram *A*, that the surface texture is not suitable for the diffraction of electrons even though the surface is crystalline. Such surfaces, when annealed at 50° C., may undergo sufficient recrystallization and/or grain growth to cause a change in the surface texture, so that an electron diffraction pattern may be obtained by transmission of the electrons through minute projections of crystals at the surface. An alternative explanation of the possible effect of annealing may be offered. Prior to annealing the crystals may be too small to be effective diffraction gratings. Annealing at 50° C. may permit growth in crystal size sufficient for effective diffraction.

The foregoing hypothetical interpretation of the significance of the diffraction effects in photograms *B*, *E* and *F* is based upon Kirchner's[21,22] generally accepted analysis* of the diffraction of electrons at the surfaces of single crystals and the adaptation of this concept to diffraction by

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[a] The relative intensities of the diffraction effects in the figure are not accurate reproductions of the original plates, owing to the necessity for controlling the printing so as to produce the clearest reproduction. The over-all density of the original plate varies from bottom to top.
[b] Composition of alloy: 4 per cent Al, 0.03 per cent Mg. balance high-purity zinc (A.S.T.M. XXIII alloy).

* Kirchner's explanation of the surface diffraction of electrons from single crystals, briefly stated, is as follows: Three conditions of diffraction may be operative. The *first condition*, giving rise to haloes, is the result of the diffraction of electrons by rows of atoms lying in the surface of the specimen and approximately parallel to the incident electron beam, while the *second condition*, giving rise to vertical lines (actually hyperbolae) on the photogram, is the result of diffraction by rows of atoms lying in the surface and perpendicular to the incident beam. A *third condition* occurs as a result of atom rows perpendicular to the surface. This gives rise to horizontal lines (actually hyperbolae) on the photogram. An intense spot appears on the photogram wherever two diffraction maxima intersect one another. Photogram *B* does not show the horizontal lines of the third diffraction condition, although *H* does show them. (Photogram *H* does not arise from the zinc surface, however, but from an organic film, as will be discussed later in the paper.)

For a complete discussion of this phenomenon, reference should be made to the original paper by F. Kirchner and H. Raether[21] or to the book by R. Beeching.[22] A discussion of the part these three conditions play in the diffraction of electrons by a highly oriented polycrystalline surface is given by R. O. Jenkins.[24]

highly oriented layers of polycrystalline material as described by R. O. Jenkins.[23,24] Jenkins observed the electron diffraction effects from polished polycrystalline graphite surfaces[23] and from oxide films on molten metals.[24] The patterns are characterized by vertical diffraction lines with intense spots at various locations along these lines. Assuming that the plane parallel to the surface is $(hkl) = (001)$ Jenkins found that the vertical maxima were due to various $(hk0)$ spacings, indicating that the crystals occupied various positions in azimuth about the normal to the (001) plane as an axis of rotation.

In the specimens of polished zinc in photograms *B*, *E* and *F*, strong zero, first and second order (the last visible only on *F*) vertical diffraction maxima were obtained from atom rows perpendicular to a (10.0) plane. The electron measured value for this atom spacing is 4.68 Å., agreeing within the limits of error with the corresponding X-ray value of 4.60 Å. Vertical diffraction maxima corresponding to the close-packed row of atoms perpendicular to a (11.0) plane are not obvious on the reproductions, although scrutiny of the original plate shows a faint indication of first order diffraction from this spacing, 2.66 Å.

The absence of diffraction spots along the central vertical maxima corresponding to Bragg reflections[25] from the basal plane may be due to the effect of refraction in destroying the sharpness of such reflections. The absence of horizontal diffraction lines in photograms *B*, *E* and *F* may be a result of the surface texture, which may not present to the incident electron beam a sufficiently long row of atoms in the direction normal to the polished surface for proper diffraction interference.

By using a very small angle of grazing incidence in photographing the electron diffraction pattern of the specimen of photogram *A*, a third halo of smaller radius than either of the other haloes is obtained. This is illustrated by photogram *C*, for which the grazing angle was 0.21°, whereas in photogram *A* the corresponding angle was 0.45°. The existence of this third halo has not hitherto been published in the literature. In a private communication, however, Dr. L. H. Germer, of the Bell Telephone Laboratories, states that he has also observed this halo.

No quantitative correlation of these three haloes with the lattice structure of zinc has been made. Calculated according to the Bragg law, these haloes correspond to interplanar spacings of 5.0, 2.46 and 1.28 Å. If it is assumed that the haloes arise from diffraction by rows of atoms lying in the surface of the specimen in the direction of the incident electron beam, calculated atom spacings of 850, 200, and 56 Å., respectively, are obtained. These spacings cannot be rationalized with the zinc crystal lattice. Such rationalization is not likely, furthermore, since the diffuse halo pattern alone has been obtained in this laboratory and elsewhere from a wide variety of surfaces. The radii of the haloes are the

same for many substances of widely different crystalline structures and atomic sizes.[12,13] Hence, an electron diffraction pattern of two or three diffuse haloes has no significance with respect to the composition of the surface being examined but appears to result in some manner from the surface texture of the deposit. In the general application of the electron diffraction technique to research investigations the photography of a diffuse-halo pattern from a surface that is almost certainly crystalline is one of the most disconcerting experimental difficulties. Before a surface will give an interpretable diffraction photogram, it must not only be crystalline but also of a suitable surface texture.

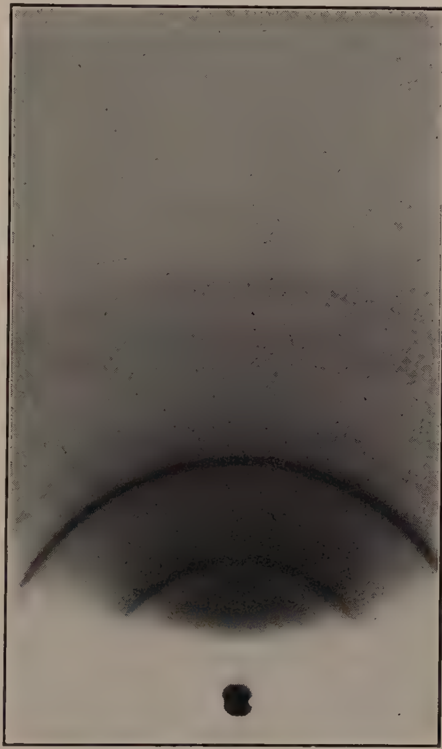

FIG. 2.—PSEUDOCUBIC ZINC OXIDE FORMED BY OXIDATION OF ZINC SURFACE.

The failure of other investigators to obtain photograms like *B*, obtained by polishing alone, may be entirely fortuitous, since in the present work very few of the many polished but unannealed specimens examined gave rise to this type of pattern. The annealing at 50° C., however, of specimens yielding only the diffuse-halo pattern generally resulted in photograms of the types *D*, *E* and *F*, with more or less clarity over a range such as is indicated from the very indistinct photogram *D* to the very definite photogram *E*.

As an illustration of complications that arose in this investigation, photograms *G* and *H* are included. These photograms were taken in an investigation of the commercial polishing procedure of buffing. Photogram *H* shows horizontal diffraction maxima, which, according to Kirchner's explanation, arise from rows of atoms normal to the surface. It was thought, at first, that these diffraction effects were from the buffed metal surface. In a letter, Dr. Germer suggested that these diffraction effects were from a film of organic material analogous to those obtained by others.[26,27,28] The specimens were washed in alcohol and in ether before they were placed in the electron camera, a treatment that was considered sufficient to remove the grease film left on the surface by the buffing compound. Subsequently it was found that by more thorough cleaning

this film could be removed. The method used was "vapor cleaning." By this procedure the specimen is suspended in ether vapor above a hot ether bath, whereupon ether condenses on the metal surface and runs off in drops, thus effecting an ether rinse with freshly distilled ether.

After removal of the organic film from the buffed specimen, the diffraction pattern most frequently obtained is that of zinc oxide. The pseudo-cubic form of zinc oxide discovered by Bragg and Darbyshire[29] is the form that most commonly occurs as a thin film on oxidized zinc surfaces.* It appears as a randomly oriented polycrystalline film, as is evidenced by the sharp Debye-Scherrer patterns of uniform intensity that are obtained. Fig. 2 is a reproduction of the photogram of a "Bragg-type oxide" film on a zinc surface. Photogram *G* of Fig. 1 is from an inadequately cleaned, buffed specimen and shows diffraction effects from the organic film as well as the underlying zinc oxide.

Ether-vapor cleaning of specimens yielding photograms of the types *B*, *E* and *F* fails to remove the material giving rise to these photograms and it is therefore concluded that the vertical diffraction maxima are not due to an organic film.

On the Possibility of Oxidation

Since the polishing was carried out by wet methods, and since the annealing was carried out in air, it might well be suspected that the specimens would oxidize under such conditions. In order to test this possibility, zinc specimens were polished on felt with extremely fine alundum abrasive suspended in petrolatum, and then annealed at 50° C. while coated with petrolatum. This treatment prevented the access of air during the polishing and annealing. The only exposure to the air was immediately before placing in the electron camera, at which time the petrolatum was removed from the specimens. Electron diffraction examination of zinc specimens polished under these nonoxidizing conditions yielded the same results as were shown by photogram *A* before annealing and *E* after annealing.

The atom spacings indicated by the vertical diffraction maxima, moreover, cannot be rationalized with the zinc oxide crystal lattice as they can be with the zinc lattice. If the diffraction effects are due to an oxide film, the crystals of the oxide film must be highly oriented. On the contrary, many cases of oxidized zinc surfaces have been encountered in this laboratory and such films have always had randomly oriented structures.

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* Since this paper was written, experimental evidence has been obtained to indicate that this corrosion film is a product of the combined action of oxygen, carbon dioxide and moisture and is not a form of zinc oxide but probably some form of basic zinc carbonate.

Buffed, polished, rolled and cast surfaces of zinc that have oxide layers of the Bragg type or of the hexagonal close-packed form always have exhibited randomly oriented polycrystalline structures in the oxide film. Even single-crystal faces of zinc that have oxidized slightly in the laboratory atmosphere show no evidence of preferred orientation in the oxide film.

From the foregoing considerations, it seems justifiable to conclude that the diffraction effects of photograms *B*, *E* and *F* are indeed due to the metallic zinc surface and not to an oxide film.

On the Effect of Annealing at 50° C.

It may be argued that the 50° C. annealing or the frictional heat of polishing may have caused an originally amorphous polished layer to crystallize. If this were true, it would not seem reasonable that an amorphous supercooled liquid would crystallize in a highly oriented fashion.

An exception to this argument could be taken if the crystalline layer beneath the polished layer were highly oriented. This might cause an amorphous metal layer to crystallize in the same orientation as the substrate metal.

Regarding the possibility of an oriented crystalline layer beneath the polished layer, two papers have been published.[8,9] With polished gold, H. G. Hopkins[8] has removed the surface of the polished metal in small increments by sputtering and has shown that after removing 10 Å. "the pattern gradually sharpens and becomes more and more intense as more and more of the surface is taken off," until the normal Debye-Scherrer diffraction pattern of randomly oriented polycrystalline gold appeared. The thickness of the Beilby layer was estimated at 30 Å. and of the total layer affected by the polishing at 400 to 500 Å. The polishing appeared to result in a gradual decrease in crystal size until only the diffuse haloes were obtained.

C. S. Lees,[9] on the other hand, also working with polished gold, found evidence of an oriented layer between the polished layer and basis metal of the original unaffected crystals. C. S. Lees concludes that the upper 20 to 40 Å. is either pseudoliquid or else is composed of minute nonoriented crystals not bigger than 15 Å. The oriented layer immediately beneath this surface layer is found to have a depth of 10,000 to 100,000 Å.

Neither Hopkins nor Lees studied polished zinc, and the writer has no experimental data on the nature of the subsurface strata of the polished specimens upon which this paper is based. The researches of Hopkins and of Lees and the results of the present paper seem to indicate that the polishing brings about a reduction in size of the crystals by the fragmentation accompanying plastic deformation. The development of a preferred orientation of the deformed crystals takes place at the same time.

Whether or not one obtains electron diffraction evidence of this oriented crystalline structure seems to depend upon the production of a surface texture suitable for the reflection type of photogram.

Summary and Conclusions

Under certain circumstances polished surfaces of zinc yield electron diffraction effects that indicate the surface to be definitely crystalline. These diffraction effects are in the form of diffraction lines perpendicular to the shadow edge of the reflection type of photogram. Quantitative correlation has been made with the hypothesis that the polished zinc surface consists of very minute crystals of zinc, oriented with their basal planes parallel to the plane of polish. Explanations for the absence of other diffraction effects that might be expected on the basis of the hypothesized structure have been offered, but these cannot be definitely proved.

Experimental evidence from this laboratory and from the literature have been adduced to show that the diffuse-halo pattern alone has no significance with respect to composition and crystalline structure of a surface, and that whether or not such a diffraction pattern is obtained is dependent on the surface texture of the specimen. No rigorous explanation can be given for the genesis of the haloes.

Acknowledgment

The author expresses appreciation to Mr. E. A. Anderson, of the Research Division, New Jersey Zinc Co., for his encouragement and counsel, and also to Dr. L. H. Germer, of the Bell Telephone Laboratories, for the benefit of his criticisms and advice. Sincere thanks are also due to Mr. W. R. Smith, who prepared most of the photograms, and to Mr. C. W. Bartholomew, who did much of the polishing.

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DISCUSSION

(*E. E. Schumacher presiding*)

C. J. Davisson,* New York, N. Y. (written discussion).—Mr. Fuller shows that some specimens of highly polished zinc give the same pattern of diffuse haloes as has been observed with a number of other metals. It was not previously known, I think, that zinc is a member of this class.

Mr. Fuller shows also that other specimens give, in addition to the haloes, a pattern of equally spaced diffuse bands lying in and parallel to the plane of incidence and that these are enhanced by mild annealing of the specimen. From the separations of these bands and other pertinent data the author calculates a crystal spacing 4.6 Å., which is $\sqrt{3}$ times the crystal constant of zinc ($a = 2.65$ Å.). He concludes from this coincidence that the surface layers contain an aggregate of small oriented crystals with their basal planes parallel to the plane of the surface, or nearly so. There is no sound basis, it seems to me, for this conclusion. There are two ways in which an aggregate of zinc crystals, oriented as Mr. Fuller assumes, could produce bands of the type observed—they might be produced by scattering from the outermost layer of atoms only, or they might be produced by scattering from a few atom layers only, from exceedingly thin crystals essentially. The scattering might be of either of these types because the angles at which the beam meets the surface is so small.

The first type of scattering would, according to my calculation, give rise to a pattern of bands corresponding to crystal spacings

$$d = \frac{\sqrt{3}a}{2(h^2 + k^2 + hk)^{1/2}}$$

where h and k are integers. The largest spacing, that for $h = 1$, $k = 0$, is $\sqrt{3}\, a/2$, or one-half the value Mr. Fuller finds.

The second type of scattering gives rise to bands corresponding to the spacings

$$d = \frac{a}{2(h^2 + k^2 + hk)^{1/2}}$$

and the largest of these is $d = a/2$; that is, again smaller than the author finds.

The distances of bands from the central band is given in the first case as

$$D = \frac{2(h^2 + k^2 + hk)^{1/2}}{\sqrt{3}}\left(\frac{L\lambda}{a}\right)$$

* Bell Telephone Laboratories.

and in the second by

$$D = 2(h^2 + k^2 + hk)^{1/2}\left(\frac{L\lambda}{a}\right)$$

All but a few of these bands might be missing, for one reason or another, but no band should appear that is not a member of one or the other of these series. Mr. Fuller's "first order" bands do not belong to either series.

I do not believe that the pattern of bands is due to zinc.

H. R. Nelson,* Columbus, Ohio (written discussion).—When a piece of zinc is abraded on successively finer grades of emery paper, ending with very light passes over No. 0000, the electron diffraction pattern shows a considerable degree of preferred orientation of the fragmented zinc crystals. The orientation is the same as that proposed by Mr. Fuller to explain his diffraction effects; viz., basal planes are parallel to the plane of the surface. After this specimen had been heated in air at about 50°C. for about 12 days, the diffraction pattern contained maxima due to the ordinary hexagonal form of zinc oxide as well as maxima due to zinc. The zinc oxide crystals were oriented exactly as were the zinc crystals, showing a definite orientation relationship between the zinc and the zinc oxide lattice. This result indicates that zinc is slowly oxidized in air at 50°C. and that possibly oxide films of sufficient thickness to obscure diffraction effects from the underlying zinc could be built up on highly polished surfaces. This possibility seems still more probable when we remember that the effective depth of penetration of the electrons is very much less on smooth, flat surfaces than it is on surfaces that are submicroscopically rough.

Moreover, there is some doubt that immersion in petrolatum will prevent a slight surface oxidation of metals. At room temperature iron oxidizes very quickly to a degree that is readily detectable by electron diffraction methods even though the oxygen partial pressure at the surface may be as low as 10^{-3} mm. If iron is abraded under benzene, then inserted in the diffraction camera while still covered with benzene, and the camera immediately exhausted, the resulting diffraction pattern still shows rings due to oxide. I have never tried this experiment with petrolatum but the International Critical Tables show the solubility of oxygen in benzene to be about the same as in paraffin oil or "Russian petroleum." The solubility is appreciable at room temperature and it would seem altogether possible that the minute quantity of oxygen necessary to form an oxide film of perhaps 10 or 20 Å. thick could readily reach the zinc surface.

I have long been impressed and somewhat chagrined by my inability to obtain interpretable diffraction patterns from polished metal surfaces. The two or three diffuse rings that usually are obtained can be explained in several different ways, a fact that explains the present state of disagreement among various workers. It seems to me, however, that adequate consideration has not been given to the possibility that the electron diffraction patterns from polished metal surfaces are not due to the metal itself but to a very thin layer of some other material covering the surface. A thin film of oxide, an adsorbed film of gas or a layer of organic molecules have been suggested as possible types of films that normally cover the surface of a metal. Very likely the metal is covered by a film of oxide on top of which is an adsorbed layer of gas. As has already been pointed out, an excessively thin film of such materials on a smooth surface would suffice to obscure the diffuse maxima diffracted from metal crystals fragmented by polishing. Germer and Storks[30] have recently shown that a single layer of organic molecules only a few carbon atoms deep

* Battelle Memorial Institute.

[30] L. H. Germer and K. H. Storks: *Jnl. Chem. Physics* (1938) **6**, 280.

gives a diffraction pattern that completely obliterates diffraction effects from the polished chromium surface on which the layer is deposited. Certainly an oxide film equally thick would be just as effective in preventing the electrons from reaching the underlying metal, and there is every reason to believe that the process of polishing is very favorable to the formation of oxides. I will venture the opinion, therefore, that few, if any, of the diffraction patterns from highly polished metal surfaces that have been reported in the literature are actually due to the metal itself.

Aside from the possibility of oxide films, still other materials sometimes appear inadvertently on the surface of specimens and give rise to patterns that are difficult to explain. Several years ago I obtained some diffraction patterns from polished iron, which are so similar to those reported by Mr. Fuller that I think they should be described here. Ingot-iron specimens were metallographically polished with levigated alumina. The diffraction patterns consisted of three diffuse haloes together with two and sometimes three or four pairs of vertical lines. The spacings corresponding to these diffraction features are summarized in Table 1.

TABLE 1.—*Electron Diffraction Patterns from Metallographically Polished Ingot-iron Surfaces*

Plate No.	Specimen and Surface Treatment	Haloes, Bragg Spacings in Ångstrom Units Corresponding to Haloes			Vertical Diffraction Lines. Spacings in Ångstrom Units between Atoms in Rows Perpendicular to Electron Beam			
		d_1	d_2	d_3	a_1	a_2	a_3	a_4
621	A19 as polished	5.3	2.4	1.24		2.64		
622	Same surface	5.0	2.3	1.27	4.52	2.58		
624	Same after degreasing treatment				4.57	2.63		1.26
623	A22 as polished		2.3	1.25	4.56	2.67	2.2	1.31
625	Same after degreasing treatment	4.8	2.3	1.23	4.52	2.61	2.2	1.30
	Mean spacings	5.0	2.3	1.25	4.54	2.63	2.2	1.29

As might be expected, the Bragg spacings corresponding to the haloes agree well with those reported by Mr. Fuller. The surprising feature, however, is the remarkable agreement between the atomic row spacings, which correspond to the vertical diffraction lines. The mean spacing calculated from the innermost pair of lines turns out to be 4.54 Å., which agrees with the zinc atomic spacing of 4.60 Å. fully as well as the 4.68 Å. value obtained by Mr. Fuller. The second pair of lines corresponds to a mean spacing of 2.63 Å., again agreeing within the limits of error with the zinc spacing of 2.66 Å. The third and fourth pairs of lines are exceedingly faint and difficult to measure. They are probably second orders of the two inner pairs of maxima. There is one obvious difference between the pattern that I have described and those obtained by Mr. Fuller. In my pattern the second pair of vertical lines is stronger than the first, whereas the reverse is true with his.

This diffraction pattern cannot be attributed to metallic iron nor to any of the known iron oxides. It is inconceivable that it can be due to zinc even though it seems to agree so well with the type of oriented zinc layer that has been hypothesized in the present paper. The pattern has not been explained, but whatever its significance it strongly suggests that the diffraction effects that have been obtained from polished zinc surfaces may not actually be due to zinc.

E. E. Schumacher,* New York, N. Y. (written discussion).—As it is only 10 or 11 years since we heard the first reports about electron diffraction studies, this paper is a reminder that progress in physical metallurgy is becoming increasingly rapid. Each year the activity in electron diffraction studies has increased, so that as a result the electron diffraction camera has now definitely established itself as a tool to aid in the solution of many metallurgical and other problems that only a short time ago appeared unsolvable.

R. Morgan,† Philadelphia, Pa. (written discussion).—Mr. Fuller is to be congratulated on his careful and elucidating study of polished zinc surfaces. As a tool in the study of surface chemistry, electron diffraction becomes more valuable by the additional information on diffuse-halo patterns.

M. L. Fuller (written discussion).—The discussion resolves itself into the question of whether or not the observed vertical diffraction maxima arise from metallic zinc. If they do arise from zinc, as I have contended, it necessarily follows that the polished surface is crystalline. If they arise from an oxide film, as is argued by Dr. Nelson, or if the mechanism of electron diffraction could not have accounted for the observed diffraction effects from zinc, as is proposed by Dr. Davisson, the conclusions of the paper are invalid.

Dr. Nelson has adduced electron diffraction observations from polished iron of a nature similar to those I have reported from zinc. Unfortunately, Dr. Nelson has not reproduced his photographs, so that a visual comparison cannot be made. While the positions of these vertical maxima from iron are similar to those obtained from zinc, they differ markedly in intensity distribution and can therefore not be considered as having arisen from the same material. Dr. Nelson has been unable to determine the origin of these diffraction effects from polished iron on the basis of metallic iron or any of the known oxides of iron. Because of this, and since I have been able to account for the diffraction effects of the present paper on the basis of the crystal lattice of zinc, I cannot agree that the evidence Dr. Nelson has adduced refutes the conclusions of this paper.

The state of the science of electron diffraction is such that explanations of the mechanism of diffraction from single-crystal surfaces and highly oriented polycrystalline surfaces have not reached the rigorous and complete understanding that has been reached in regard to X-ray diffraction. In my analysis of the diffraction effects obtained in this paper, I have considered the diffraction maxima as arising from one-dimensional gratings of rows of atoms in the basal plane of zinc and thus accounted for the observations on the basis of metallic zinc. In adopting this viewpoint, I have followed the work of F. Kirchner and of R. O. Jenkins (ref. on page 257). On the other hand, Dr. Davisson has stated that this interpretation as applied to the work of this paper is unsound. Dr. Davisson has advanced an alternative explanation, which indicates that the observed diffraction maxima could not have arisen from metallic zinc. No explanation, however, has been offered by Dr. Davisson to account for the observations on the basis of his analysis of the diffraction effects.

It seems to me that a completely satisfying solution of the problem must await general positive agreement as to the genesis of the diffraction effects reported here and the similar effects found by Dr. Nelson from polished iron. In opposition to the interpretation and conclusions in the present paper, there have been brought forth arguments to show that the diffraction effects could not have arisen from metallic zinc, but nothing has been offered to lead to a positive explanation of their origin from something other than zinc.

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* Bell Telephone Laboratories.

† University of Pennsylvania.

Pure Zinc—Its Preparation and Some Examples of Influence of Minor Constituents

By E. C. Truesdale* and Gerald Edmunds,* Member A.I.M.E.

(New York Meeting, February, 1939)

A few years ago H. M. Cyr, working in the Research Laboratories of The New Jersey Zinc Co., produced a few pounds of zinc[1] of such purity that no other elements were detected in it by spectrographic analysis, using the facilities then available. This zinc contained less than one ten-thousandth of one per cent of metallic impurities.[2] During the decade that followed upon the laboratory production of this "spectrographically pure" zinc, commercial developments brought about the production of large tonnages of zinc of purity exceeding 99.99 per cent, and today zinc of 99.999 per cent purity is produced and marketed as "chemically pure" zinc. Typical analyses of present supplies of high-purity zinc are given in Table 1.

Table 1.—*Typical Analyses*

Zinc	Percentage by Weight				Sum of Pb, Fe, Cd
	Pb	Fe	Cd	Al	
Special High Grade[a]	0.007[b]	0.005[b]	0.005[b]	none	0.010[b]
C.P. (chemically pure)	<0.0002	0.0005[c]	0.000052		
S.P. (spectrographically pure)	<0.0002[d]		<0.00005[d]		

[a] A.S.T.M. Standard Specification for Special High Grade Slab Zinc (A.S.T.M. Designation: B 6-37).

[b] Maximum.

[c] Fe chemically determined. Pb and Cd are spectrographically determined.

[d] Differences between composition of C.P. and S.P. zinc are discussed later in this paper.

The availability of commercial tonnages of special high-grade zinc has been the basis for the development of the zinc-base die-casting alloy industry which, in the year 1936, consumed one-eighth of the zinc used in the United States for all purposes. This and the C.P. and S.P. grades have given impetus to scientific investigations into the properties of pure

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* Investigator, Research Division, The New Jersey Zinc Co., Palmerton, Pa.

[1] H. M. Cyr: Pure Zinc. *Trans.* Amer. Electrochem. Soc. (1927) **52**, 349.

[2] Nonmetallics are not considered; none are known to be present.

zinc and the effects of both natural and intentional alloying ingredients. Later in this paper some of these subjects will be considered but first a discussion will be given of the method of production of the purest zinc and the important matters of analysis and contamination.

Preparation of Spectrographically Pure Zinc

The method of preparation is that of vacuum distillation of liquid zinc, the vapor being condensed directly to the solid state on a graphite

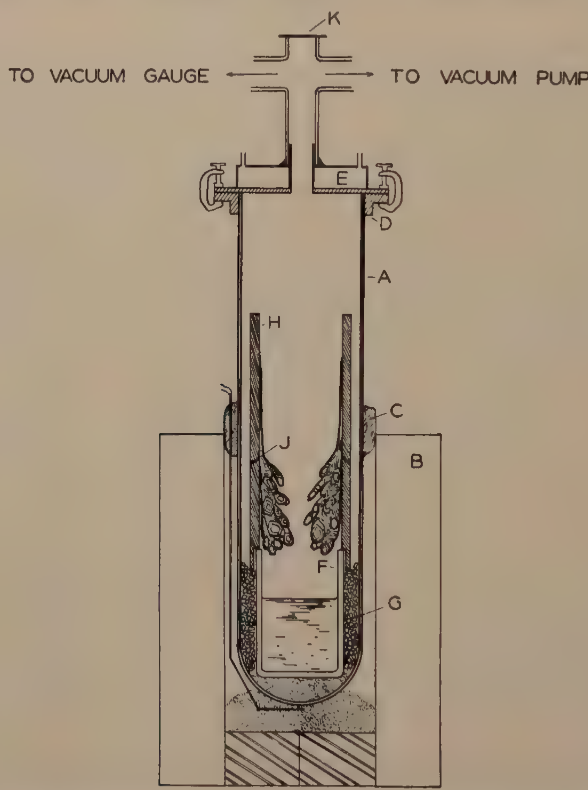

Fig. 1.—Apparatus for production of spectrographically pure zinc.

sleeve from which it can readily be removed. The method first described by H. M. Cyr[1] is still in use, but details of design and operation of the apparatus have been varied from time to time by various operators, and the description given in the following paragraphs applies to the method at present in use.

A sketch of the apparatus is shown in Fig. 1. The Pyrex tube A is about $5\frac{1}{2}$ in. in diameter by 24 in. long, with a wall thickness of $\frac{1}{4}$ in. It rests on sand in an electric furnace B, which is wound so as to be hotter at the bottom than at the top. The tube is held in place by asbestos wool packing C. The flanged brass collar D is sealed on with wax, and

the flanged, water-cooled brass head E is held on by a number of clamps. Three concentric grooves in the flanged surfaces are filled with wax to insure a vacuum-tight joint. The charge of zinc is contained in a heavy-walled Pyrex pot F, which rests on sand. The space between A and F is filled with pieces of pure copper G, to promote the conduction of heat to the charge, a process that otherwise would be slow in an evacuated system. Contamination of the product by vaporization of this copper is hindered by the position of the graphite sleeve H; copper frequently is detected spectrographically in the zinc produced, but only as an extremely faint trace, and there is some question whether the copper is in the zinc or in the graphite electrodes.

The graphite sleeve, on which the zinc condenses, is cut vertically into three sections to facilitate subsequent removal of condensate, and during a run these sections are wired together. Each section of the sleeve is also cut horizontally at J. These discontinuities increase the resistance to the flow of heat upward along the sleeve, and as a result the portion below J remains too hot for direct condensation of zinc on the sleevs. The zinc then condenses immediately above J and the bright crystals grow down into the lower portion of the sleeve without adhering to it or to the upper edge of the glass pot. Most of the cadmium in the metal being distilled, together with some zinc, condenses on the upper part of both the sleeve and the tube as a dull, powdery deposit. The part of the tube extending above the furnace is cooled by an electric fan.

Sleeves of materials other than graphite have been tried, since the graphite absorbs large volumes of gas that cannot be completely pumped off, but in spite of this difficulty the graphite is still preferred. New sleeves require baking out at a red heat to remove various volatile impurities.

In starting a run, the assembly is heated while open to the air until the charge has melted, thus ensuring good thermal contact between the pot and the charge. This results in the formation of a film of oxide over the liquid metal surface, which probably decreases the subsequent rate of evaporation somewhat. Melting in a hydrogen atmosphere decreases but does not eliminate this film formation.

When the charge has melted, the system is evacuated by means of a laboratory oil pump. Continuous pumping results in a smooth deposit of zinc, which is difficult to handle, and formation of a nodular deposit is promoted by intermittent pumping. Pumping periods of an hour, with rest periods of from one to several hours (e.g., overnight) have been found satisfactory. The pressure, measured by a thermocouple vacuum gauge, varies between 0.01 and 0.3 mm. of mercury. This pressure variation has been observed, through the window K, to result in considerable sublimation and recondensation of the lower portions of the zinc deposit, and this is believed to be the chief cause of the nodular growth obtained.

The furnace temperature is held at about 570° C. as measured by a thermocouple on which the tube *A* rests. The temperature at the upper end of the furnace is about 100° lower. The temperature of the molten zinc is then about 460° when evacuation is begun, and probably decreases somewhat as evaporation proceeds.

Under these conditions, a charge of 3000 grams of zinc will be 85 per cent distilled in 24 hr., and about 50 per cent of the total charge will be recoverable as desirable crystals. About half of the remainder of the deposit, while not in useful form, is sufficiently pure to be added to later charges. The powdery deposit, containing most of the distilled cadmium, and the residue, containing most of the lead and iron, are discarded.

The product is redistilled, if necessary, until the present technique for qualitative spectrographic analysis shows only the *raie ultime* (by arc spectrum) of lead (wave length 2833 Å.) and sometimes the *raie ultime* of cadmium (wave length 2288 Å.) and/or of copper (wave length 3247 Å.), and none of these more than very faintly.

The present lower limits in this laboratory for the quantitative spectrographic estimation of impurities in zinc are, in per cent: Cd, 0.00005; Pb, 0.0002; Fe, 0.001. This high limit for iron seems to be due to the atmospheric contamination found in every industrial or semi-industrial location. Under more favorable conditions a lower Fe limit has occasionally been reached. The average of a large number of chemical analyses of C.P. zinc gives 0.0005 per cent Fe, and this value is accepted for this grade of zinc. Hence, in a quantitative sense, all that can be said is that the concentrations of impurities in S.P. zinc are lower than the limits stated above, but this is misleading because the qualitative test is more sensitive than the quantitative one and the qualitative test detects only extremely faint traces of the impurities mentioned in the preceding paragraph. This may be further emphasized by pointing out that a special lot of C.P. zinc, which is the starting material for the preparation of S.P. zinc, itself carries the following impurity concentration: Cd. 0.000027 per cent and Pb, 0.0001 per cent by spectrographic analysis, and Fe, 0.0005 per cent by chemical analysis.

In obtaining the spectrographic analysis of the above-mentioned special lot of C.P. zinc, the impurities were concentrated before analysis, by treating the zinc with sulphuric acid sufficient to dissolve only about 90 per cent of the sample. This results in reprecipitation of heavy metal impurities on the remaining zinc, and the latter is then used as the spectrographic sample. The same method is being tried with S.P. zinc, but the rate of solution of this zinc in sulphuric acid is so extremely slow that no results have been obtained.

Great care is exercised throughout the preparation and handling of the pure grades of zinc to prevent contamination during or subsequent to manufacture. Minute amounts of contaminants are sufficient to multiply the impurity content of such pure material by several fold. Hands,

tools and containers are kept scrupulously clean and the metal is protected from dust as well as possible. Melting is usually done in Pyrex glass or silica containers, and no detectable impurities are thereby introduced. Notwithstanding the care that is used, contamination occasionally occurs, as is evident from reanalysis. This point can hardly be emphasized too strongly, particularly when individuals not accustomed to such pure materials are engaged in work with them. Alloys made from a pure zinc base may be seriously contaminated by impurities in the addition metal.

Physical Constants of Purest Zinc

The physical constants of purest zinc were published on page 281 of the March 1938 issue of *Metal Progress* and will not be reviewed here. As is pointed out there, the purity stated is that for metal used in preparing test pieces. Actual compositions may have differed significantly owing to contamination during handling and preparation of specimens.

Some Effects of Small Amounts of Other Metals on Properties of Zinc

The effects of minor natural impurities in zinc on the properties of zinc-base die-casting alloys, and the powerful influence of other metals in partly overcoming these effects, are well known, and need only be reviewed here.

Nearly all modern zinc-base die castings contain aluminum, magnesium and sometimes copper as principal alloying ingredients. Binary zinc-aluminum alloys when pure are highly resistant to corrosion. A few thousandths of one per cent of lead, cadmium, or tin, however, will cause severe corrosion of an intergranular type, which results in expansion or disintegration of the alloy during exposure to warm, humid atmospheres. The presence of a few hundredths of one per cent of magnesium or certain other metals prevents this corrosion provided the impurity contents do not exceed the limits set by the A.S.T.M. Tentative Specification for Zinc-base Alloy Die Castings (Table 2).

Table 2.—*Chemical Composition of Zinc-base Alloy Die Castings*
A.S.T.M. Designation: B 86-38 T

Constituent	Alloy XXI	Alloy XXIII	Alloy XXV
Copper, per cent	2.5–3.5	0.10 max.	0.75–1.25
Aluminum, per cent	3.5–4.5	3.5–4.3	3.5–4.3
Magnesium, per cent	0.02–0.10	0.03–0.08	0.02–0.08
Iron, maximum, per cent	0.100	0.100	0.100
Lead, maximum, per cent	0.007	0.007	0.007
Cadmium, maximum, per cent	0.005	0.005	0.005
Tin, maximum, per cent	0.005	0.005	0.002
Zinc, per cent	remainder	remainder	remainder

Specimen A2677 Specimen A2678

FIG. 2.—EDGE OF COMPRESSION-TEST SPECIMENS TESTED AT 25° C. × 1.5.

Specimen A2677 Specimen A2678

FIG. 3.—EDGE OF COMPRESSION-TEST SPECIMENS TESTED AT 130° C. × 1.5.

Specimen A2677 Specimen A2678

FIG. 4.—EDGE OF COMPRESSION-TEST SPECIMENS TESTED AT 175° C. × 1.5.

Specimen A2677 Specimen A2678

FIG. 5.—EDGE OF COMPRESSION-TEST SPECIMENS TESTED AT 200° C. × 1.5.

Magnesium likewise has a powerful influence on the creep strength of rolled zinc-copper alloys containing about one per cent of copper. An addition of 0.006 per cent of magnesium to this alloy increases its creep strength by more than 50 per cent.

E. A. Anderson, of the Research Laboratories of The New Jersey Zinc Co., a few years ago carried out an interesting and heretofore unpublished investigation on the influence of small additions of various metals to zinc on the tendency of the resultant alloys to crack when compressed at various temperatures.

The general procedure used was to prepare the alloy in the form of

Specimen A2677 Specimen A2678

FIG. 6.—EDGE OF COMPRESSION-TEST SPECIMENS TESTED AT 225° C. × 1.5.

chill-cast cylinders, ⅞ in. in diameter by 1½ in. long, the ends having been machined flat and parallel. These cylinders were placed between parallel, flat steel plates in a constant-temperature oil bath and compressed axially until they were one-half or one-fourth as long as before compression. The compression speed was 3 in. per minute. Only a few of the many specimens tested will be illustrated here.

In one series of tests, two grades of zinc, with no added alloy additions, were compared. The analyses of the actual specimens, *after* being used for compression tests, are given in Table 3.

TABLE 3.—*Analyses of Specimens of Unalloyed Zinc after Usage in Compression Tests*

Designation	Weight Per Cent Zinc by Difference	Analyzed Impurity Content,[a] Per Cent by Weight		
		Pb	Fe	Cd
A2677	99.999	0.0002	0.0007	0.00005
A2678	99.989	0.0012	0.006	0.0035

[a] No elements other than those reported were detected by the sensitive qualitative spectrographic method.

Specimen A2677 Specimen A2678

FIG. 7.—EDGE OF COMPRESSION-TEST SPECIMENS TESTED AT 250° C. × 1.5.

Figs. 2 to 7 show the edges of the cylinders after compression at a rate of 3 in. per minute to one-fourth of their original thickness at temperatures of 25°, 130°, 175°, 200°, 225° and 250° C.

The edges were considerably roughened and a few minute compression cracks (which do not show well on the photographs) appeared on the purer grade of zinc, A2677, tested at temperatures of 25°, 130° and 175° C. At the higher testing temperatures the edges were even rougher, but no cracks were evident. The specimens appeared to have developed

compression failure cracks during early stages of compression, which later healed. In marked contrast, as is clearly evident in the photographs, the slightly less pure grade of zinc, A2678, exhibited numerous

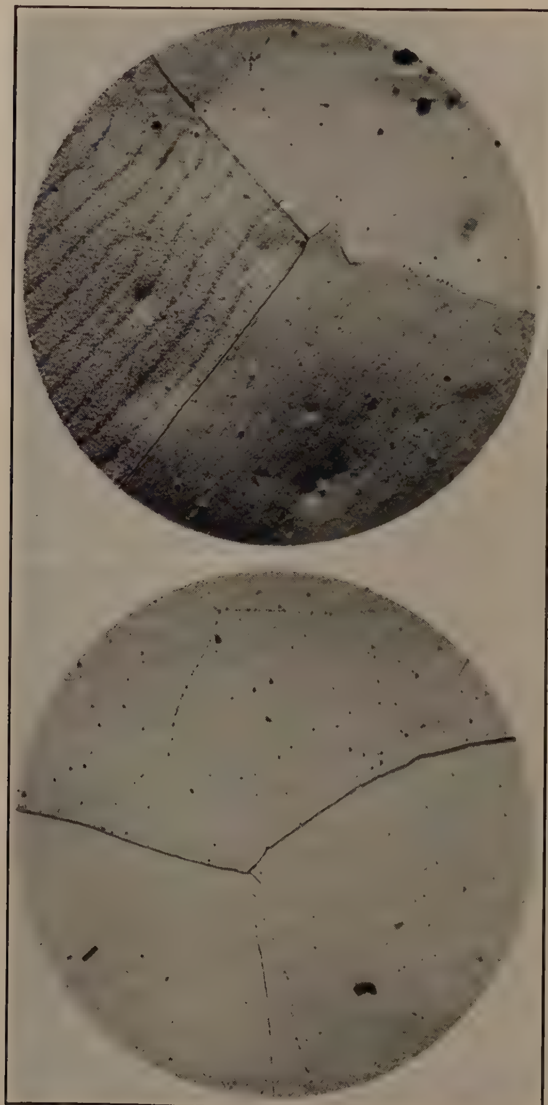

Fig. 8.—Special High Grade zinc, unalloyed. Analyzed 0.0001 per cent Cu.
Fig. 9.—Special High Grade zinc alloyed with copper. Analyzed 0.0019 per cent Cu.
Chill cast, metallographically polished, etched 10 sec. with a solution of 1.5 grams Na_2SO_4, 20 grams CrO_3, 100 c.c. water. Photographed with polarized, oblique illumination. × 100.

large compression cracks after testing at all six temperatures. It was not determined whether only one or more of the impurities present in the A2678 zinc was responsible for the observed difference, but since the total difference in composition of the two grades of zinc was only 0.01

per cent, the significance of minute amounts of other constituents is clearly important.

A striking example of the effect of a contaminant in an alloying element appeared during compression studies on a series of zinc-lead alloys containing various amounts of lead up to 1.2 per cent. Unusually serious cracking was noted, which later was found to be due to traces of bismuth contained in the lead supply. In this instance the bismuth content of the lead was 0.02 per cent, and the corresponding bismuth contamination of the alloy having the highest lead content (1.2 per cent Pb) was only 0.00024 per cent. One alloy of this series, with a calculated bismuth contamination of only 0.00006 per cent, was noticeably affected.

Another example of the remarkable effect of a minor constituent arose recently during comparative micrographic examination of Special High Grade zinc and an alloy of 0.0019 per cent of copper with the same lot of metal. A prominent subgrain boundary (dendritic) structure appeared in castings of the alloy (Fig. 9) but not in the unalloyed zinc (Fig. 8). The development of this substructure is apparently a coring effect, but it is surprising to find it arising from the presence of as little as 0.0019 per cent of copper. The coring presumably is due to the solidus temperature of zinc-rich zinc-copper alloys changing only minutely with concentration. The substructure is readily effaced by annealing.

Summary

A method of preparing spectrographically pure zinc has been described in detail. Examples have been given of the influence of minor constituents, both natural and added, on compression failure of zinc, and of a trace of copper on the microstructure of zinc. Attention has been called to the influence of magnesium upon the corrosion resistance and creep strength of certain zinc alloys.

Acknowledgment

The authors are indebted to Messrs. H. M. Cyr and E. A. Anderson for a large part of the experimental evidence, to Messrs. M. L. Fuller and G. W. Standen for most of the analytical work, and to Mr. E. A. Anderson for his counsel.

DISCUSSION

M. G. Corson,* New York, N. Y. (written discussion).—It is of course pleasant to know that zinc of so high a purity as that described by Messrs. Truesdale and Edmunds is now available. Nevertheless, certain statements in their paper (obviously not original with the authors) do not seem to tally with the *possible* facts.

There is, for instance, the question of contaminations in the die-cast zinc-base alloys. It is stated and long accepted by the American Society for Testing Materials as a sort of gospel that lead, cadmium and tin do account for severe intercrystalline

* Consulting Metallurgist.

corrosion of these alloys. It is well known that the electrochemical differences between zinc and the metals mentioned are very small—mere hundredths or even thousandths of a volt. On the other hand, a great part of the volume of die-cast alloy articles is occupied by a very intimate mixture of zinc and a high aluminum constituent. We do not define the latter more clearly inasmuch as its nature is not yet well established. At any rate the electrochemical differences between the two constituents of these intimate eutectoidlike mixture must be high, running into at least some tenths of one volt. A high electrochemical difference does not necessarily imply a high intensity of corrosion phenomena, because its influence may be checked by a number of causes. On the other hand, a low electrochemical difference is simply unable to start a decent amount of corrosion. Moreover, copper is quite a regular element in die-cast alloys and iron cannot be avoided. Both of these must be—from the theoretical viewpoint at least—just as bad if not worse than cadmium, lead or tin.

I foresee the reply that "from the practical viewpoint" this is exactly what happens. However, I refuse to be convinced. Why? Simply because the influence of these three elements was never scientifically reported. The only thing we have as evidence of this detrimental influence of these three impurities is hearsay, lest some producers of zinc or die-casting alloys possess plenty of data not available to the metallurgical fraternity.

What happens in fact, I believe, is something of this kind: A die-cast article corrodes. It is analyzed (the sound articles are not) and 0.01 per cent lead is found. In a few minutes of time, it is suspected, indicted, convicted and condemned. At another time, corrosion occurs and a customer complains. No lead is found but the eager-to-serve chemist reports 0.01 per cent cadmium or tin. The procedure is repeated and a verdict of guilt is rendered.

I do not expect anyone to try to convince me, for I am not a prospective buyer of die-cast articles, not even in the remotest future, but I would suggest that in the interest of truth at least 100 test pieces be produced by die-casting from each of four alloys, one pure and three others contaminated with 0.01 per cent cadmium, lead and tin, respectively. If then, in a rapid corrosion test, the first series remains practically intact, while the great majority (say 90 per cent) of the other three series fail, not even a confirmed sceptic could voice his doubts. In the absence of such conclusive *statistically* conducted tests the question of the desired purity must remain open. I also doubt the real absence of nonmetallic impurities. Small amounts of sulphur and oxygen are extremely difficult to detect and to measure, and a tiny particle of sulphide here or there or an incidental film of oxide might account for failure observed in a more logical manner.

These objections cover also the statement by the authors that one sample was noticeably affected (on the basis of the mechanical test) because it contained a calculated amount of 1/1,500,000 of bismuth. Did the authors look for some other possible culprit?

Incidentally, Fig. 9 cannot show a coring effect, for the amount of copper present is really too slight. A more plausible explanation would be the precipitation of a phase approximating $CuZn_5$ in chains of fine particles along some preferred direction, an electrochemical action starting at the contact surfaces of these chains. As a parallel case: The presence of as much as 0.002 per cent oxygen in copper produces a definite network of lines along the precipitation chains of copper monoxide.

G. Edmunds (written discussion).—In considering the influence of minor constituents upon zinc and its alloys, five examples have been given. In each case the effects were asserted to have been observed. The detailed information required to substantiate these assertions was not given, since to do so would have required unwarranted lengthening of the paper. Mr. Corson has objected to two of these

assertions, but, as in the original paper, we feel it would be out of place in this discussion to supply, as could be done from A.S.T.M. committee reports and private data from our own and other laboratories, proof that the influences of impurities on the expansion of zinc-aluminum alloys in humid atmospheres are as stated. Proof could likewise be furnished for the statement concerning bismuth.

In regard to Fig. 9, we have stated that the "substructure is apparently a coring effect." Mr. Corson says it "cannot be a coring effect" and supplies what he claims is a "more plausible explanation," "the precipitation of a phase approximating $CuZn_5$." Examination of the accepted equilibrium diagram for zinc-rich zinc-copper alloys should convince one that such an explanation is untenable.

The Supposed High-temperature Polymorphism of Tin

By C. W. Mason,* Member, and G. E. Pellissier, Jr.,† Student Associate A.I.M.E.

(New York Meeting, February, 1939)

Tin has long been cited as offering a classic example of polymorphism, second in repute only to the allotropy of sulphur. The notorious "tin disease," which Cohen[1] has studied so exhaustively in terms of the enantiotropic transformation of tetragonal white β tin to cubic gray α tin, has apparently encouraged the expectation that one or more additional polymorphic modifications might exist. The search for confirmation of this idea has, as might be anticipated, led to the accumulation of a body of miscellaneous evidence, much of which would probably never have been sought, or taken seriously even by its discoverers, but for previous assumptions.

The ball apparently was started rolling in 1880 by Trechmann,[2] who reported a new modification of tin (γ tin), which was brittle and found in "hard head," a highly arsenical, slaggy material produced in a certain stage of tin smelting. A mixture of two kinds of crystals was obtained from a Cornish tin furnace, and those thought to be γ tin were studied crystallographically. The results indicated that these crystals were rhombic and of different density from the tetragonal tin prepared electrolytically by Miller.[3] Their analysis was given as 98.7 per cent Sn, 1.3 per cent Fe, and traces of As, Sb, Bi and S. In 1881 von Foullon[4] obtained similar crystals from a Bohemian tin furnace. Headden[5] examined crystals similar to those of Trechmann and von Foullon and reported them to be monoclinic, but of analysis corresponding to stannous sulphide. Later, Stevanovic,[6] by goniometric measurements, proved that these crystals of SnS were really rhombic.

Groth[7] pictures and describes both "rhombic tin" (Fig. 9, vol. 1) and stannous sulphide (Fig. 84, vol. 1); their faces and angles correspond within the accuracy of measurement.

Spencer[8] in 1921 examined the above evidence critically; he found similar crystals from Cornish tin furnaces, proved them to be SnS, and even was able to analyze some of Trechmann's original specimens, finding high sulphur content. (Apparently Trechmann's analysis had been based on a second lot of crystals, not described crystallographically.)

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* Professor, Chemical Microscopy and Metallography, Cornell University, Ithaca, N. Y.

† International Nickel Company Fellow, Department of Metallurgy, Carnegie Institute of Technology, Pittsburgh, Pa.; formerly Graduate Student, Cornell University.

[1] References are at the end of the paper.

The foregoing represents the sole evidence the authors have been able to find for an orthorhombic third modification of tin; the crystal system is correct, *but* the material was undoubtedly stannous sulphide and not tin. If there is a third modification of tin, as has been claimed on other grounds, the absurdity of calling it orthorhombic should have been apparent to the various later investigators who have felt the need for a label for a new field in a phase diagram.

And even if Trechmann had actually found rhombic tin, it is not justifiable to assume that this phase would necessarily be the one obtained under the conditions of other investigations, or that changes in various physical properties necessarily involve or are due to any change in crystal system.

The only other crystallographic evidence for a third polymorphic modification of tin is that of von Simson,[9] who obtained a hexagonal phase in the course of an X-ray study of a series of tin amalgams at room temperature. She states: "Tetragonal tin dissolves less than 2 per cent mercury. Therefore, since the tetragonal lattice disappears between 6 per cent and 8 per cent mercury, one can conclude that the hexagonal lattice contains approximately 12 atoms of tin to one atom of mercury," which indicates a Sn-Hg intermetallic compound, but is not, and was not proposed as evidence of any allotropic transformation at elevated temperature. Guertler[10] is responsible for calling this tin-rich phase a high-temperature modification of tin and indicating it on a field of a tentative Sn-Hg diagram, apparently on the basis of six-rayed surface patterns on cast tin-rich amalgam reported by Puschin.[11] Later X-ray work by Stenbeck[12] confirms the above hexagonal structure in the range of 6 to 10 per cent Hg, but neither he, nor Hansen[13] in reviewing the work on the Sn-Hg system, considers that this is any indication of a high-temperature modification in tin.

The remainder of the evidence proposed for a third polymorphic modification of tin is not crystallographic, but is indirect, being based upon discontinuities of various physical properties at elevated temperatures.

Discontinuities have been observed by various workers at 127°, 120° to 200°, 161°, 165°, 170°, 175°, 170° to 195°, 186°, 190°, 195°, 200° and 203° C., all of which have been proposed as transformation temperatures. γ tin is shown in the pressure-temperature diagram for tin,[14,15] and in many of the binary diagrams with tin[15–18] usually at 161° C., although no crystallographic proof, X-ray or microscopical, has yet been presented—which is reminiscent of β iron, but less defensible. The physical properties of "γ tin" are given in the usual sources of chemical and metallurgical information,[19–22] as though it were a phase in unquestionably good standing.

Tammann[23] concluded that an abrupt decrease in extrusion velocity at 203° C. indicated a transformation.

Tyte[24] considers differences in the fracture and plasticity of tin above and below 180°, explained in terms of single and double gliding, to confirm Tammann's $\beta \rightarrow \gamma$ transformation at 203° but Chalmers, in discussion, criticizes the lack of evidence as regards purity, orientation, and grain growth, and questions the existence of any discontinuity on the basis of the author's numerical data.

Cohen and Goldschmidt[25] found that electrolytically prepared tin varied considerably in specific gravity, depending on the current density used, and concluded that such variations are not indicative of the existence of γ tin. Furthermore, their dilatometric measurements failed to yield any evidence of an allotropic transformation.

Degens[26] found a discontinuous volume increase at 161° C., under a pressure of 1 kg. per sq. cm. Matuyama[27] performed a similar experiment, using a differential dilatometer and tin of high purity, and found no such discontinuity.

Smits and de Leeuw,[28] working with tin amalgams, reported an abrupt change in volume, which they attributed to the $\beta \rightarrow \gamma$ transformation; the transformation temperature obtained by extrapolation was 200° C.

Werner[29] observed a break in the electrical resistance-temperature curve at 161° C.; this observation is not in agreement with the more precise determinations by Matuyama[27] and Murphy.[30]

Jänecke[31] concludes, from a gradual change in the shape of the pressure-time (temperature) curve, that tin (purity not stated) undergoes an allotropic transformation at 186° C. on heating (196° C. on cooling). The experimental procedure was similar to that used in obtaining *P-T* curves, except that the pressure was unidirectional. The melting point as determined by this method was found to be considerably lower (217° C.) than the accepted melting point of tin (232° C.).

Smits and Spuyman[32] found breaks at 200° C. in the electromotive force-temperature curves of two thermocouples. Matuyama found no such breaks.

Travers and Huot[33] found a break in the dilatometric curve in the neighborhood of 165° C. in certain cases only. Using a calorimetric method (not described), a marked discontinuity in the curve was found in some cases at 170° to 171° C.; irregularity of the appearance of this discontinuity was associated with a difference in thermal history of the specimens, without specific explanation. Jaeger and Bottema[51] found a discontinuity in specific heat and explain it on the basis of a rhombic tin existing above 203° C.

Goodrich[34] obtained a small, abrupt change in the specific volume of 99.8 per cent pure tin near 160° C. Matuyama,[27] using an apparatus with a sensibility 400 times as great, failed to detect any such abrupt change.

Goetz,[35] in photoelectric measurements, found a change in his curve in the region 180° to 100° C. This effect might well be due to the precipitation of small amounts of impurities, or to surface changes on recrystallization or oxidation, to which the photoelectric effect is sensitive.

J. Shinoda[36] found two breaks at 195° and 175° C. in the differential thermal analysis curve, and a weak discontinuity at 203° C. in the electrical resistance-temperature curve of tin.

In an article concerning the allotropy of tin, Tammann[14] presented a pressure-temperature diagram in which rhombic tin was allotted a definite field of stability, on the basis of some of the earlier work, already shown to be of doubtful significance. Further, he stated that the transformation into rhombic tin can lead to cracks and fissures on hot-rolling or pressing. Stolba[48] had previously shown that at about 200° tin, like other metals near their melting points, becomes brittle enough to be pulverized in a mortar, but Smits[37] attributed this hot-shortness to a modification stable above 200°. Greaves and Jones[55] found a change of direction of the impact-temperature curve (no more marked than in copper at 120° to 200°) at 190°.

Homer and Plummer, in a recent study of the embrittlement of tin at elevated temperatures,[54] demonstrate the marked influence of very small amounts of impurities on the temperature above which brittle fracture occurs. They also confirm the linear hardness-temperature relationship previously found by Sauerwald,[53] in contradiction of earlier work by Ludwik.[54]

Whatever the methods of investigation used, it should be emphasized that there is a considerable step between the observation of discontinuities in physical properties and the interpretation of them as due to polymorphic transformations rather than to other possible causes. Such

inferential reasoning might be legitimate, if the existence of a high-temperature modification of tin were first actually established on crystallographic evidence, either microscopical or X-ray. But without such evidence any "breaks" in the various temperature-property curves, even if occurring at similar temperatures, are only more or less unrelated observations on samples of different purities; each should be explained on the grounds most appropriate to it, rather than to be mustered, often in a most haphazard array, as proof of a phase transformation and of polymorphism, of which the most inherent and fundamental proof is still lacking.

In addition to the unconvincing character of the evidence for γ tin already cited, negative experimental results by various workers are significant.

Mügge[38] was perhaps the first to show that the microscopical structure and twinning lamellae of tetragonal tin persisted above 161° C., which indicates, but does not prove, the nonexistence of γ tin.

Nishikawa and Asahara[39] in an early X-ray study of the recrystallization of several rolled metals, found no radical change in the diffraction patterns of white tin (purity not stated) at high temperatures, and concluded that no transformation occurred. Murphy,[30] using sensitive measuring methods and "Chempur" tin, found no arrest in the heating or cooling curves for tin between 20° and 232° C. Electrical resistance-temperature curves over this temperature range also showed no inflections. Hanson and Pell-Walpole,[40] in agreement with the findings of Murphy, discovered no evidence of the allotropy of tin at elevated temperatures. In this laboratory, Forgeng* failed to find any evidence of a temperature arrest on heating and cooling samples of structurally pure tin from 232° C. to room temperature.

Obinata and Schmid[56] found unchanged diffraction patterns at about 200°, and no indications of polymorphism from studies of the mechanism of extension of single crystals of tin, between 20° and 200°.

The most conclusive research concerning the alleged high-temperature allotropy of tin was conducted by Matuyama.[27] The following impurities were reported for the tin used: 0.01 per cent Zn, 0.008 per cent Pb and a trace of Cd. No breaks were found in: the electrical resistance-temperature curve, the differential dilatation-temperature curve, the differential thermal analysis curve, and the thermoelectromotive force-temperature curve. Even more convincing evidence of the absence of any high-temperature allotropy of tin was provided by the identity of good X-ray powder patterns taken at room temperature and at 220° to 223° C. Furthermore, X-ray patterns of a 4 per cent Cd alloy (a small amount of cadmium is supposed by some to accelerate the transformation to γ tin) taken at room temperature and at 152° to 163° C. were also identical.

Honda[41] has reviewed this work briefly and pointed out its importance, in an attempt to dispel the general belief in the high-temperature allotropy of tin.

Neuberger,[50] in a later summary of work on allotropy, also accepts Matuyama's findings as conclusive.

Homer and Plummer's review of the evidence regarding γ tin[52] (which reached the present authors just as the final revision of this manuscript was about to be mailed) discusses in considerable detail much of the work mentioned above, and shows how discontinuities in physical properties can well be due to impurities. The conclusion is positively against the existence of any high-temperature polymorphism.

* Private communication to the authors.

Discussion of Experimental Procedure

In an investigation of polymorphism, the primary concern is the selection of an experimental procedure that will indicate with certainty the presence or absence of a polymorphic change. The following definition has been offered by Sosman[42] as covering all the generally recognized cases of polymorphism:

> That quality of a crystalline substance which permits it to appear in modifications belonging to different classes of symmetry, or differing in axial ratio or in specific volume to a degree not explainable by ordinary thermal dilatation or elastic compressibility [or by the presence of foreign atoms in solid solution in the parent lattice].

Since the introduction of X-ray analysis, a phase change involving distinct and unique lattice patterns has been tacitly accepted as the criterion of polymorphism.

Such a change in lattice configuration is naturally reflected in changes in its physical, mechanical, chemical and electrical properties, and a study of these properties might be resorted to in a study of polymorphism. Unfortunately there are several objections to this method of investigation:

1. The changes may be of small magnitude and difficult to detect.
2. Experimental difficulties in measuring these properties at elevated temperatures are encountered. Room-temperature measurements may be impossible because of the uncertainty of retaining the high-temperature modification by quenching.
3. One or more of the physical properties of the different modifications of the same substance may be nearly equal.
4. The interpretation of discontinuities in certain property curves is seriously complicated by the presence of impurities, and by previous thermal or mechanical treatment, grain size and orientation.
5. The properties may change more or less abruptly without a change in lattice pattern.

X-ray analysis, however, offers a method largely free from these objections, since it measures directly the arrangement and spacing of the atoms:

1. Slight changes in lattice symmetry or atomic spacing may be detected.
2. Studies at elevated temperatures obviate the need of quenching.
3. Small amounts of impurities result in only a slight change in atomic spacing in the parent lattice.
4. Elastic deformation or differences in grain size result merely in changes in the breadth of the lines in the X-ray pattern.

It follows, also, from the direct nature of the X-ray method that negative results are considerably more conclusive than when the indirect methods are used, for there is always the possibility that a polymorphic change is occurring without appreciably affecting the property under investigation.

It has been stated by Moesveld[43] that the nonexistence of allotropy in a particular case can never be proved, because of possible suspension

of the transformation in finite time. Although numerous cases of suspended transformations are known in metals, the metastable forms exist only at rather low temperatures, at which the atomic mobility, and consequently the rate of transformation, is low. The temperatures at which the $\beta \rightarrow \gamma$ transformation supposedly occurs in tin are relatively high with respect to the melting point and also in view of the fact that active grain growth occurs well below 100° C.

The presence of a certain impurity in solid solution in a given solvent metal lattice, in amount exceeding some critical percentage, may cause a change in the symmetry of the solvent lattice (intermetallic compound formation) at constant temperature or with change of temperature. Moreover, it is conceivable that the presence of such an impurity in lesser amount than this critical percentage may cause an order-disorder change in the symmetry of the lattice at elevated temperatures. Moesveld[43] claims that, in investigations of allotropy, the purity of the metal, within limits, is not important, but Cohen[1] recognizes the marked influence of the amount and distribution of small amounts of impurities such as bismuth, as shown by Mason and Forgeng.[45] In the present investigation it was considered essential to use, both on theoretical and practical grounds, only the purest tin available.

A "powder oscillation," back-reflection method was used; a beam of X-rays impinged on an oscillating massive polycrystalline sample of tin and the reflections in the region $\theta = 75°$ to $90°$ were recorded on a photographic film. The chief advantage of this method is its sensitivity in detecting slight changes in the crystal structure of a metal by means of a rather simple apparatus and technique, and with minimum error from any inaccuracy of dimensional measurements. Other advantages are facility in heating of the sample, and the possibility of measuring accurately the temperature of the specimen.

The resulting pattern resembled a powder pattern, although the diffraction rings were nonuniform in intensity and some were incomplete, owing to the large grain size of the sample. This was not objectionable, because the intensities were not utilized and the diameters of the rings could still be measured with sufficient precision.

Chill-cast unworked specimens were used, but it was evident from the high-temperature photographs and from visual examination that considerable grain growth (resulting in fewer reflections) did occur during the 8-hr. heating interval. For this reason, newly cast specimens were necessary for each run at the higher temperatures. The number of reflections observed at these high temperatures was considered sufficient, however, to indicate any change in the crystal structure, since it is impossible to imagine any change in symmetry or axial ratio that would leave unaltered the markedly different high-index planes represented.

A film of palm oil (used in hot-tinning), on the face of the specimen exposed to the X-ray beam, served as adequate protection of the metal

against oxidation, without decomposing seriously or impairing the intensities of the diffracted X-rays by absorption or scattering.

It was found that 200° C. was the maximum temperature to which the front face of the specimen could safely be raised without danger of melting the portion of the specimen inside the furnace, owing to the existence of a temperature gradient.

Experimental Procedure

X-ray Diffraction Experiments

Material.—Structurally pure tin, previously prepared electrolytically by Forgeng[45] in this laboratory, was used.* As far as the authors know,

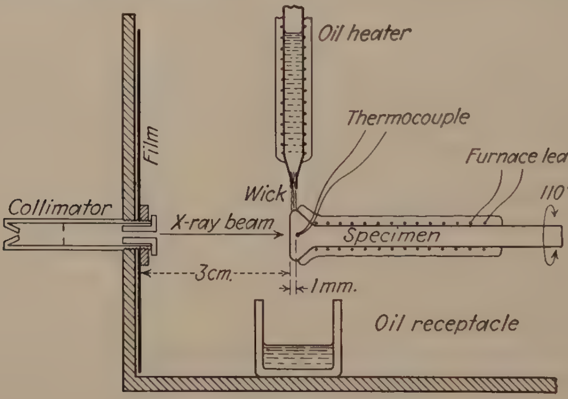

FIG. 1.—DIAGRAM OF CAMERA.

this is the purest tin available. It is free from the microstructure common to all commercial and reagent grades of tin. A previous spectrographic examination showed that this tin contained small amounts of copper, lead and iron. The "Chempur" tin used for comparison purposes was the Standard Sample 42B of the Bureau of Standards, of analysis: bismuth, 0.0035 per cent; copper, 0.0017; lead, 0.0035; iron, 0.0017; antimony, 0.0018. Sulphur, arsenic and zinc not detected.

Preparation of Specimens.—The tin was melted in a beaker under palm oil and was poured, at a temperature of 300° C., into a cold, split graphite mold. The mold contained a cylindrical cavity 3 in. deep and 5⁄16 in. in diameter, conical at the top end. A thermocouple was arranged in the mold, prior to pouring, so that it would be cast into the metal, with the junction about 1 mm. below the surface of the solidified meniscus.

The surface of the meniscus was ground flat successively on metallographic emery papers Nos. 1, 0, 00 and 000. A small furnace was then constructed around the stem of the specimen, using asbestos paper and 6 ft. of No. 28 enameled chromel wire as the heating element.

* Prepared by electrolysis of a solution of 250 grams C.P. $SnCl_2{\cdot}2H_2$ (Baker or Kahlbaum) in 1000 c.c. of water containing 10 c.c. concentrated HNO_3. This method is used by Cohen and his coworkers in their recent investigations.[1]

Apparatus (Fig. 1).—The source of X-rays used in this investigation was a gas-discharge tube of the self-rectifying type, equipped with a copper target. The tube was operated at a voltage of 40 kv. and an amperage of 20 ma. A filter was omitted to shorten the exposure. The back-reflection camera used, except for the oscillation mechanism, was similar to the conventional type.[46]

Because of the heating element and thermocouple leads, a rotation through 360° was not feasible; 110° oscillation by means of a 1-r.p.m. synchronous motor was used. A thrust bearing insured a constant distance of 3.0 cm. ± 0.5 mm., from film to specimen. The specimen was supported at one end in a chuck equipped with three set screws.

The X-ray film (5 by 7 in.) was enclosed in a light-tight black paper envelope. The film was attached to the back of the camera by means of a nut fitted to a threaded projection of the collimating tube, which projected through a hole in the film. It was found that cooling of the film during the high-temperature exposures was not necessary.

A film of palm oil was supplied continuously to the face of the specimen by means of a woolen wick, in contact with the beveled edge of the specimen face and carried in the drawn end of a vertical glass tube 12 in. long and ½ in. in diameter, in which the oil was preheated to the temperature of the specimen.

The temperature of the face of the specimen was measured to about 0.2° C. by means of a calibrated iron-constantan thermocouple (No. 28 wire) and potentiometer. Actual temperatures at the face of the specimen were checked by means of organic compounds of known melting points, and found to correspond with the readings from the thermocouple, within the constancy of temperature maintained.

Procedure.—X-ray exposures were made with the specimen at the following temperatures: 25°, 80°, 100°, 150°, 180° and 200°, respectively. Temperature readings were taken every 15 min. in the high-temperature runs, and the fluctuations were found to be only ±1 to ±3° C.

From measurements of the diameters of the rings in the resulting X-ray patterns, it was possible to compute the values of the interplanar spacings corresponding to these reflections, in the conventional way. These reflections were then identified by comparing the observed values of the interplanar spacings d with similar values calculated from the known lattice constants of β tin, $a = 5.8195$, $c = 3.1750$.[49]

Results.—The left-hand column of Table 1 gives the calculated values, excluding those which structure factor calculations showed to be of zero intensity. The quantitative data appear in Table 1.

The results shown by way of illustration in the table are all based on single runs, the same specimen being used at various temperatures until its grains grew too coarse. Duplicate runs with other specimens, especially at the higher temperatures, gave fewer lines, but in each one of the patterns the diameter of at least one diffraction ring (usually more

TABLE 1.—*Quantitative Results*

Indices	Calculated Planar Spacings, d	25° C., 6 Hours Observed Values of d			80° C., 8 Hours Observed Values of d			100° C., 7 Hours Observed Values of d			150° C., 7½ Hours Observed Values of d			180° C., 8 Hours Observed Values of d			200° C., 8 Hours Observed Values of d		
		K_{α_1}	K_{α_2}	K_{β_1}	K_{α_1}	K_{α_2}	K_{β_1}	K_{α_1}	K_{α_2}	K_{β_1}	K_{α_1}	K_{α_2}	K_{β_1}	K_{α_1}	K_{α_2}	K_{β_1}	K_{α_1}	K_{α_2}	K_{β_1}
033	0.929																0.928		
620	0.920													0.920	0.922				
611	0.916													0.914			0.913	0.915	
233	0.885	0.884	0.884		0.883			0.884			0.885	0.886							
541	0.874	0.873	0.875					0.872			0.872	0.873		0.874	0.875		0.875	0.876	
143	0.847	0.846			0.846			0.846			0.846								
532	0.845	0.844	0.845		0.844	0.845		0.844	0.845		0.844	0.845							
631	0.837	0.837	0.838								0.836						0.837	0.838	
640	0.807	0.808	0.809					0.808						0.808	0.809		0.806		
701	0.804													0.804		0.804			
004	0.794	0.794	0.795		0.794			0.794	0.796		0.794								
433, 503	0.783	0.783	0.784		0.784	0.785		0.784	0.785		0.783	0.785							
721	0.775				0.776											0.776			
224	0.740			0.741			0.740			0.740									
613	0.710												0.710						
741	0.704			0.704															

than one) could be measured directly and used to check the radii of incomplete rings appearing in the same pattern.

All of the observed reflections, without exception, were positively identified as reflections derived from the known lattice of tetragonal tin. The intervals between the calculated values of d were large enough, and the accuracy of the observed values great enough, to show real, and not merely probable, coincidence. Moreover, it was found that for all observed reflections the structure factor was greater than zero, and that no reflections appeared for which the structure factor was zero.

Most of the K_α reflections theoretically possible, in the region studied, were observed in one or another of the X-ray patterns obtained. A few K_β reflections were observed because of the absence of a filter in the path of the X-ray beam. Their presence was incidental, although they made possible the identification of certain planes having K_α reflections outside of the back-reflection region investigated.

Because of the high resolving power in this region, the K_α doublet appeared as two separate and distinct rings (K_{α_1} and K_{α_2}).

Discussion of X-ray Results.—The results of several runs at 25° C. indicated that the procedure gave values of the interplanar spacing, for any specific plane, which were consistent and in agreement with those calculated. No measurable changes in the interplanar spacings occurred at any temperature from 25° to 200° C. This means, of course, that no change in the symmetry or axial ratio of the tetragonal tin lattice had occurred in this temperature range. This is considered as positive and conclusive evidence of the nonexistence of an allotropic transformation of tin between 25° and 200° C.

The present results are in agreement with the X-ray findings of Nishikawa and Asahara,[39] Obinata and Schmid,[56] and Matuyama,[27] but are considered, because of their quantitative nature, to be of considerably more significance in proving that tin undergoes no high-temperature transformation.

In spite of the slight difference in purity between the structurally pure tin and the Chempur tin, the results obtained in the two cases were identical, and demonstrate that Chempur tin, which is generally used in metallographic investigations of tin, likewise undergoes no transformation at elevated temperatures.

The interplanar spacings did not change appreciably with temperature. Calculations indicate that the changes would be within the limits of the experimental variations. This in no way affects the conclusions drawn above, because any changes resulting from a transformation would certainly be of a different order of magnitude.

Microscopical Examination at Elevated Temperatures

The structurally pure tin, previously described, was melted in a beaker under palm oil and poured out on a cold alberene table top, where it

solidified immediately. Buttons with a bright meniscus (1 in. or more in diameter and 1/8 in. thick) were obtained, in a number of attempts, which were smooth and free from oxide or other serious surface imperfections. Because of the purity of the tin and the rapidity of cooling, the usual "sink-head" was not present.

A calibrated iron-constantan thermocouple was cast in the specimen at the time of pouring.

Protection of the meniscus surface against oxidation at elevated temperatures was effected by means of a drop of palm oil pressed out under a cover glass on this surface. At temperatures above 50° C. the palm oil exerted a mild etching effect on the metal surface; it was possible, therefore, to follow the progress of grain growth and to detect, by continuous etching, any microstructural changes that might be occurring at elevated temperatures.

Apparatus.—The specimen was heated on an electrical hot stage. The temperature of the specimen was controlled, and measured and checked at its surface, by the methods used for the X-ray studies.

The specimen was observed by means of an upright metallographic microscope, and photographed by a Makam camera (Leitz).

Procedure and Results.—The specimen was first heated to about 40° C. in order to melt the palm oil and drive off water and air present in the oil. At this temperature, photomicrographs were taken of several locations on the surface of the specimen. The temperature was then raised slowly, during a period of 1 hr., to 200° C., with the specimen under constant observation. No change in microstructure, other than normal grain growth, was detected. In order to eliminate the possibility of a suspended transformation, the specimen was held at about 200° C. for 8 hr. Frequent observations during this period indicated that grain growth was proceeding normally, and that otherwise the microstructure of the specimen remained unaltered. At the end of this 8-hr. heating interval, photomicrographs were taken of the identical locations photographed at 40° C.

Discussion of Results.—The original cast surface of the specimen was smooth, and the grain boundaries were well defined. The high-temperature photographs showed that no roughening of the surface, such as would be expected if any discontinuous volume change, due to a transformation, occurred during the prolonged heating interval. In many fields absolutely no change in the microstructure occurred on heating, even to incipient melting.

Grain Growth on Annealing without Deformation

The fact that unworked cast pure metals rarely if ever exhibit grain growth on heating is rather generally accepted.[48] Even when the specimen was handled so as to avoid the slightest deformation, grain growth was noted in some fields; it could be observed at temperatures well

below 100° C., if time was sufficient. It is possible that trapped cooling stresses, accentuated by the tetragonal character of tin, were responsible. The grain growth did not indicate any new type of structure, but its existence might well be expected to encourage nucleation or development of any possible polymorphic modification at the grain boundaries, and to guarantee the absence of any "suspended transformation on a rising heat" if such could be conceived to exist.

Summary

1. No valid crystallographic evidence exists for rhombic or any other γ tin.

2. Discontinuous changes in physical properties with temperature are not proof of polymorphism.

3. Careful investigations, based on X-rays and physical properties, have failed to find any evidence for γ tin.

4. Back-reflection powder X-ray photographs of pure tin, at several temperatures between 25° and 200°, and at atmospheric pressure, show no indication of any structure but that of tetragonal β tin.

5. A simple apparatus for taking these photographs is described.

6. Microscopical observation at temperatures up to the melting point reveals no structural changes except grain growth.

7. Grain growth occurs, at temperatures well below 100°, in cast tin carefully protected from any external deformation.

Acknowledgment

The authors are indebted to Prof. C. C. Murdock, of the Department of Physics, Cornell University, for helpful suggestions and for advice in connection with the calculations, and to Prof. J. L. Hoard, of the Department of Chemistry, for the use of the X-ray tube.

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DISCUSSION

(*B. W. Gonser presiding*)

C. E. Homer and H. Plummer,* Greenford, Middlesex, England (written discussion).—We are interested to see that the X-ray work described in the paper by Messrs.

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* International Tin Research and Development Council.

Mason and Pellissier has confirmed the absence of polymorphism in tin at elevated temperatures, since we had previously come to the same conclusion from rather more indirect evidence (ref. 52). It is unfortunate, however, that the authors' X-ray experiments could be carried only up to 200° C., since a few papers report change points at slightly higher temperatures. We feel certain from the evidence now available that γ tin does not exist, but if the present work was intended to settle the question permanently, it should have covered a temperature range greater than that in which transformations have been recorded. As it is, the result is less conclusive than the earlier X-ray investigation of Matuyama, who worked up to 223° C.

G. Derge,* Pittsburgh, Pa. (written discussion).—I want to emphasize the need for this investigation. In listing the standard references that accept gamma tin, the authors have left untrodden a good many rather prominent toes which were definitely in the path. The contemporaneous presentation of this paper and that of Homer and Plummer, to which the authors have referred, should impress serious metallurgists with the fact that at present there is no valid evidence for the existence of gamma tin.

It is regrettable that time limitations prevented the extension of the X-ray study to the temperature range between 200° C. and the melting point. However, the microscopic examination, coupled with the work of Homer and Plummer and the other experimental evidence presented from the literature, places the burden of proof on the side of those who propose to explain their troubles with gamma tin. The tin research being conducted in the Metals Research Laboratory at the Carnegie Institute of Technology has not disclosed any phenomena that would indicate a high-temperature transformation in tin. This statement includes some recent work which has been done with material of a somewhat higher purity than that used by the authors. This tin is thought to be at least six nines pure and has been described elsewhere in these meetings.

C. W. Mason (written discussion).—The authors fully realize the desirability of obtaining X-ray data in the range 200° to 232° C. The gradient in the furnace was such that the heated portion of the sample melted if the surface temperatures were raised much above 200° C. If a suitable source of vertically incident radiation had been available, the surface of the specimen could have been studied up to incipient fusion, as was done microscopically.

The significance of this latter evidence might be emphasized, for it proves the absence below the melting point of any polymorphic transformation of a sort involving a visible change in grain structure. Longitudinal sections of the X-ray specimens, in which a gradient up to the melting point had been maintained for 8 hr. or more, also showed no indication at any point of structural changes other than grain growth.

* Metals Research Laboratory, Carnegie Institute of Technology.

Studies upon the Corrosion of Tin, II—The Effects of Other Anions in Carbonate Solutions

By Gerhard Derge,* Junior Member A.I.M.E., and Harold Markus*

(Detroit Meeting, October, 1938)

The introductory paper[1] of this series described the potential behavior of tin in sodium carbonate and bicarbonate solutions whose pH ranged from 8.4 to 11.2 and demonstrated that significant and reproducible results could be obtained by proper attention to experimental technique. In examining the corrosion of tin under such conditions, it is desirable to know the effects of anions, aside from carbonate, that are likely to be present in commercial materials packaged in tin. Therefore, in this paper the potential behavior of tin in carbonate solutions to which sodium fluoride, chloride, bromide, iodide, sulphate, nitrate, monobasic phosphate, dichromate, perborate and acetate have been added will be described. For most of the additions, solutions containing 0.001 and 0.01 moles of the added material were studied. The experimental procedure was exactly the same as that described in the first paper; the pH of the electrolyte was controlled by adjusting the ratio of carbonate to bicarbonate as follows:

	pH
0.1 M $NaHCO_3$	8.4
2 parts 0.1 M $NaHCO_3$, 1 part 0.1 M Na_2CO_3	9.5
1 part 0.1 M $NaHCO_3$, 2 parts 0.1 M Na_2CO_3	10.0
0.1 M Na_2CO_3	11.2

The reagents used were all of C.P. grade.

The anions studied may be divided into three groups: (1) anions that had little or no effect upon the potential curves—sulphate, nitrate, and acetate; (2) those that helped to prevent corrosion at low pH only—fluoride, chloride, bromide, and iodide; (3) those that helped to prevent corrosion at high pH also—phosphate, perborate, and chromate.

Potential Measurements†

The time-potential curves representative of group 1 are shown in Fig. 1. These are the curves for 0.005 M sulphate ion and their similarity

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* Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

[1] References are at the end of the paper.

† As in the first paper,[1] all potential values are referred to a saturated calomel cell as zero, with noble metals like silver negative; i.e., increasing positive values indicate a greater tendency to corrode.

to the curves for the corresponding pure carbonate solutions without added ions is very marked (refer to Fig. 4 in the first paper[1]). With a pH of 10 or less, there is more tendency for the potential to fall with time than in the sulphate-free solutions, but this is not a major effect. The curves of Fig. 1 are also representative of the action of the other ions of group 1, nitrate and acetate.

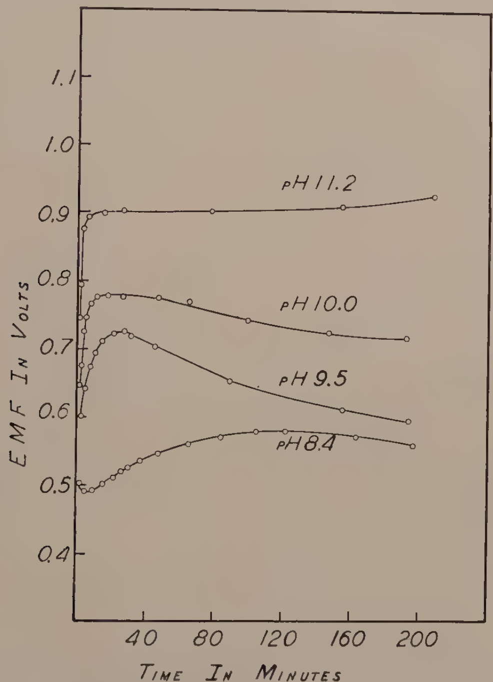

FIG. 1.—TIME-POTENTIAL CURVES IN PRESENCE OF SULPHATE ION. 0.005 M Na_2SO_4 added to carbonate solutions of the pH indicated.

The curves of Fig. 2 for 0.01 M chloride ion show exceptional passivity in solutions with a pH of 9.5. This was entirely unexpected, since earlier experiments in 0.001 M chloride solutions gave no indications of such an effect. The curves for fluoride, bromide and iodide are similar to those for chloride, though the passive tendency at pH 9.5 is not so marked. The fluoride, bromide and iodide ions also differ from chloride ions in that their passivating effect becomes apparent in 0.001 M solutions. Typical curves demonstrating these features are shown in Fig. 3. The protective action of the chloride ion will be discussed more completely in a later section of the paper.

The time-potential curves for phosphate, perborate and chromate ions are shown in Fig. 4, and it is apparent that even in solutions with a pH of 11.2 the 0.01 molar solutions of these ions have a marked tendency to lower the activity of the metal; in fact, even 0.001 molar chromate has

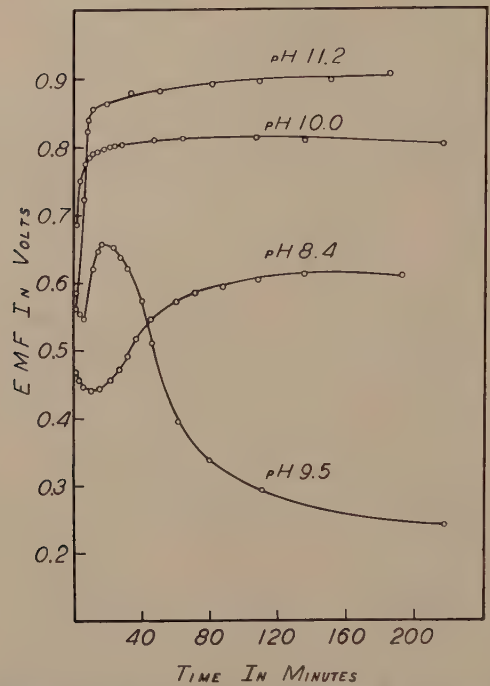

FIG. 2.—TIME-POTENTIAL CURVES IN PRESENCE OF CHLORIDE ION. 0.01 M NaCl added to carbonate solutions of the pH indicated.

TABLE 1.—*Weight Loss of Pure Tin in Carbonate Solutions*

Sample No.	Solution	pH	Days Immersed	Weight Loss, Grams
15	0.1 M Na_2CO_3	11.2	9	0.0449
16	0.1 M Na_2CO_3		9	0.0403
17	0.1 M Na_2CO_3		9	0.0448
19	2:1 $CO_3^{=}:HCO_3^{-}$	10.0	9	0.0188
20	2:1 $CO_3^{=}:HCO_3^{-}$		9	0.0204
21	2:1 $CO_3^{=}:HCO_3^{-}$		9	0.0172
10	0.1 M Na_2CO_3	11.2	15	0.0593
12	0.1 M Na_2CO_3		15	0.0592
13	0.1 M Na_2CO_3		15	0.0576
18	2:1 $CO_3^{=}:HCO_3^{-}$	10.0	15	0.0343
23	2:1 $CO_3^{=}:HCO_3^{-}$		15	0.0330
28	2:1 $CO_3^{=}:HCO_3^{-}$		15	0.0285

some influence at this pH. The sample of 0.01 M perborate solution at first became passive at a pH as high as 11.2, but after 4 hr. the normal potential for this alkalinity was reached. To all appearances the protective action was due to a film of oxygen on the surface of the specimen, and the protection vanished when the excess oxygen of the perborate was used up. Of the ions studied, chromate and phosphate are the only ones that permanently diminish the tin potential in such strongly alkaline solutions.

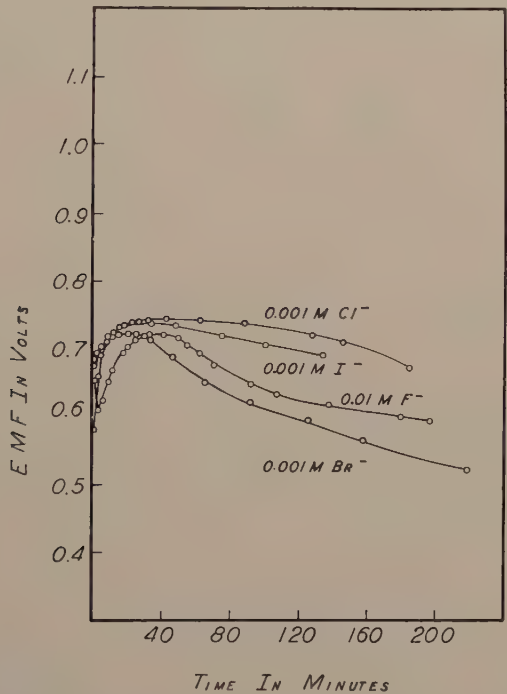

FIG. 3.—TIME-POTENTIAL CURVES IN PRESENCE OF HALIDE IONS IN CARBONATE SOLUTIONS WITH pH OF 9.5.

WEIGHT-LOSS EXPERIMENTS

To supplement the potential measurements, weight-loss studies were made in the series of carbonate solutions. The specimens were prepared exactly the same as for the potential work, except that they were rolled to a thickness of 0.5 mm. and cut into rectangles 7 by 2.5 sq. cm. One end of the weighed sample was rolled around a Pyrex rod, which was rested on top of a 100-c.c. beaker and held in place with beeswax so that a surface 10 by 2.5 sq. cm. was exposed to the solution. These beakers were placed in large glass containers, similar to those in which the potential measurements were made. Air, cleaned as for the potential measurements, was drawn through each container, and then they were sealed and placed in a

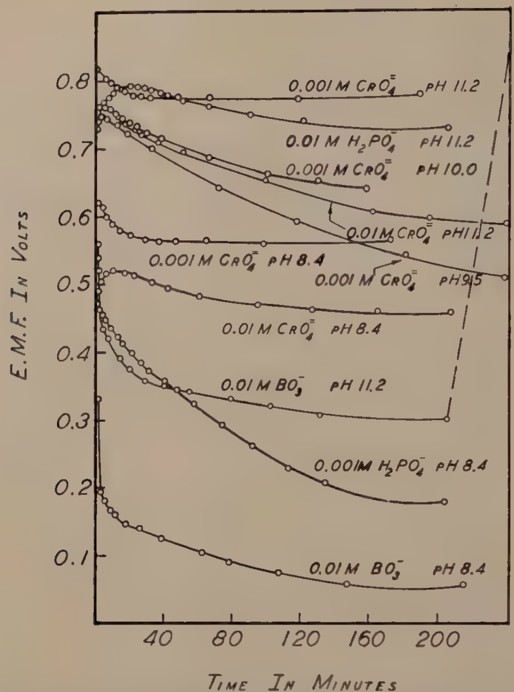

FIG. 4.—TIME-POTENTIAL CURVES IN PRESENCE OF PHOSPHATE, PERBORATE, AND CHROMATE IONS.

Typical curves are shown for 0.01 and 0.001 M additions of these ions.

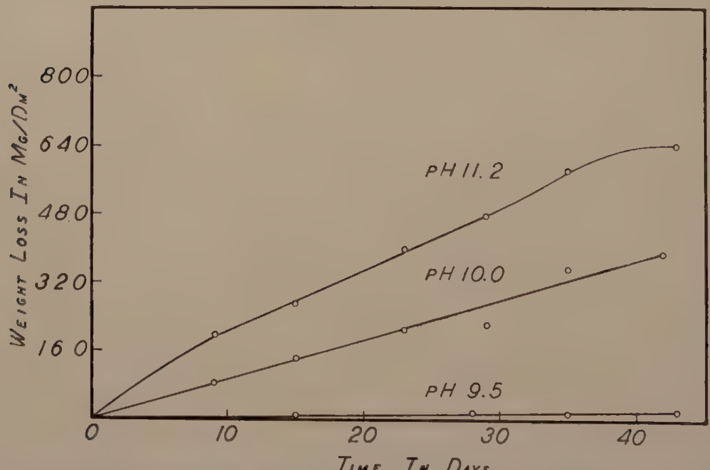

FIG. 5.—WEIGHT-LOSS CURVES FOR PURE TIN, SHOWING DEPENDENCE UPON pH IN CARBONATE SOLUTIONS

constant-temperature room at 25.8 ± 0.2° C. At chosen intervals of time, samples were withdrawn and cleaned for weighing by making them cathode for a few minutes in a 0.1 M Na_2CO_3 solution, using a platinum anode and an e.m.f. of about five volts. Three samples of a kind were removed at a time. Typical data are shown in Table 1. The generally good agreement, as well as the reproducibility of the potential measurements, made additional samples seem unnecessary. After 45 days, no weight loss could be detected in the bicarbonate solutions (pH 8.4). Graphs showing weight loss against time are given for the higher pH solutions in Fig. 5.

It is significant that the weight-loss results correspond to those that would be predicted from the potential measurements alone. This is also true for the other conditions under which weight-loss measurements have been made, examples of which are given in the next section of this paper.

Effectiveness of Protective Films

The potential behavior of 0.01 M chloride solutions of pH 9.5 has led to some interesting exploratory experiments. The most likely explanation of the protection this solution gives the tin is the formation of an insoluble oxychloride film. The formation of such tin compounds is familiar to analytical chemists, and Scholder[2] has shown that in general the stability of amphoteric metal hydroxides such as $Sn(OH)_4$ is increased when the hydroxyl ions are partly replaced by chloride. Bryan[3] showed that the corrosion of tin in citric acid is retarded by the addition of 2 per cent NaCl, and that this effect is more pronounced when the samples have not been freshly abraded. Some experiments were therefore designed to develop oxychloride films and observe their behavior.

One set of samples was allowed to stand in a solution of 0.01 M Cl^- in carbonate with pH 9.5 for 24 hr. The potential behavior of this electrolyte is shown in Fig. 2. These were then transferred to various carbonate

Table 2.—*Stability of Oxychloride Films*
(Formed by immersing samples for 24 hr. in a carbonate solution with pH 9.5 which was 0.01 M with NaCl.)

Electrolyte	pH	Result
1. 0.1 M $NaHCO_3$ + 0.01 M NaCl	8.4	Remained passive for 81 days.[a]
2. 2:1 $CO_3^=$:HCO_3^- + 0.01 M NaCl	10.0	Remained passive for 16 days.[a]
3. 0.1 M Na_2CO_3 + 0.01 M NaCl	11.2	Became active after 100 min.
4. 0.1 M $NaHCO_3$	8.4	Remained passive for 74 days.[a]

[a] Experiment discontinued at this time.

electrolytes and their potentials followed. The results are tabulated in Table 2, and show that films formed in such a manner are stable in a pH range from 8.4 to 10.0.

A set of 10 samples cut from a commercial tube alloy, about 1 per cent copper, was kept for 90 days in individual beakers containing the electrolyte 0.01 M Cl^- in carbonate with a pH of 9.5, using the technique described in the preceding section. At the end of this test no visible signs of corrosion were evident, and no weight loss could be detected. Without cleaning, five of these were transferred to solutions with a pH of 11.2 and the other five to a pH of 8.4, and after 136 days no evidence of corrosion has appeared in any sample.

Additional weight-loss experiments have been made with Chempur tin in solutions with a pH of 11.2 containing 0.01 M $Na_2Cr_2O_7$. After 50 days of immersion, no evidence of corrosion has appeared. Preliminary weight-loss tests in carbonate solutions containing phosphate indicate that this ion does not offer as much protection as chromate.

These tests indicate that the films produced in 0.01 Cl^- solutions with a pH of 9.5 and in 0.01 $Na_2Cr_2O_7$ solutions with a pH of 11.2 have the characteristics of thinness, tenacity, permanence, and complete coverage, which are required for satisfactory protection.

Conclusions

There are some rather striking observations to be made from the data given in this paper. It is generally known that tin is corroded in alkaline solutions, whereas it is comparatively resistant to corrosion in nearly neutral solutions (see Fig. 4 of the first paper). However, it is significant that in carbonate solutions small amounts of foreign anions all tend to lessen this corrosion tendency, or at least have no deleterious effects, if the pH can be kept below 9.5. Experiments in nearly neutral solutions of 0.1 M alkali salts of a large number of acids led T. P. Hoar[4] to the same conclusion, though his conditions were somewhat different because he studied the salts individually rather than in the presence of carbonate. At a pH of about 10.0 the foreign anions have a very slight effect, except phosphate, perborate and chromate. This indicates that some attention to the pH of carbonate products should lengthen package life, and that often harmless additions of some anion can be made that will actually afford a large measure of protection. These studies indicate that protective films may be formed in halide, chromate, perborate, and phosphate solutions, and further experiments investigating the possibilities of these films are now in progress. The marked similarity in behavior of the halide ions has also been noted.

Summary

1. Time-potential curves have been made for sodium fluoride, chloride, bromide, iodide, sulphate, nitrate, phosphate, chromate, perborate, and acetate, in concentrations of 0.001 and 0.01 moles per liter in carbonate solutions with a pH range from 8.4 to 11.2.

2. Weight-loss measurements in selected cases from the solutions mentioned were of the order predicted by the potential measurements.

3. Films developed in 0.01 M chloride solutions with a pH of 9.5 and in chromate solutions provide appreciable protection against alkaline corrosion.

Acknowledgments

The Bristol-Myers Company, of New York City, has sponsored the research program of which this investigation is a part.

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The Plastic Flow of Metals

By C. W. Mac Gregor,* Member A.I.M.E.

(Detroit Meeting, October, 1938)

The observation of the flow layers, or Lüders' lines, produced in mild steel when it is stressed into the plastic range often provides considerable useful information for the study of the fundamental mechanism of the plastic flow of metals. It is a commonly observed fact that as soon as the upper yield point in a mild-steel tensile-test bar is passed, an unstable condition develops in the equilibrium, the load on the testing machine drops and if the surface of the bar contains a thin mill scale, the latter begins to flake off rapidly along certain "lines." These "lines" are in reality traces of wedge-shaped flow layers and are formed by the intersection of the surface of slip and the surface of the bar. The average plane of the flow layer itself has been found by various experimenters to be inclined at an angle of approximately 45° to the axis of the test bar. In a body of more complicated shape stressed in possibly a different manner, the tangent planes to the flow layers at each point seem in many cases to be inclined at an angle of about 45° to the principal stress directions at the point. As examples of the latter may be mentioned the logarithmic spirals obtained when a rivet hole is punched in a thin plate, or when a tube is subjected to internal pressure only, etc. Hence if the flow layers are observed from an experiment, the shear-stress trajectories —the curves indicating the directions of the maximum shearing stresses in the body—may then be approximately determined. Since the latter curves form an orthogonal family inclined at 45° to the principal stress directions, the family of principal stress trajectories, or the curves indicating the directions of the principal stresses, may be thus obtained.

Although the discontinuous type of stress-strain curve at the yield point is commonly observed with test bars of mild steel, more recent experiments have shown that this is by no means the only material exhibiting this interesting phenomenon. A similar effect has been observed in zinc and cadmium crystals, by Becker and Orowan;[1] in duralumin and other aluminum alloys, by Dawidenkow,[2] Elam,[3] Fell[4] and others; in copper and copper-alloy crystals, by Elam;[5] in brass by Elam;[5] in brass wires by deForest;[6] in higher carbon steels, tungsten steel, and

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* Associate Professor in Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

[1] References are at the end of the paper.

nickel steels at certain temperatures and straining speeds, by Yuasa,[7] and in single crystals of iron, by Gensamer.[8] Some of these materials showed successive discontinuous yieldings when tested with very precise equipment for certain temperatures during the entire yielding range from initial plastic flow to fracture. This has led some investigators recently to the conclusion that possibly all plastic flow occurs in a stepwise discontinuous manner and that this type flow is not restricted to mild steel alone. Indeed, flow layers have also been observed in many of the above mentioned materials, which have a similar appearance to those obtained in mild steel.

It is then apparent that studies of the mechanism of plastic flow will throw considerable light on the entire field of plastic flow if carried out on mild steel, in which flow layers are easy to produce.

The reasons for this discontinuous behavior in yielding do not seem to be entirely clear at present. Certain theories have been advanced to account for the phenomenon of the upper and lower yield points in mild steel and the subsequent flow process. Among the easiest to visualize is that suggested by Nádai,[9] in which the individual crystals of the aggregate are supposed to be encompassed by thin layers of cementite forming a brittle skeleton framework around the soft ferrite grains. As soon as the upper yield load is reached, the framework is considered as collapsing, owing to a local stress-concentration, and transferring the load to the soft ferrite crystals, which immediately yield plastically. This hypothesis has recently been critisized by Fell[4] and others on the basis that flow layers and an upper yield point continue to exist for materials in which such a cementite boundary is almost negligible in size. Fell attributes the formation of such localized layers solely to the properties of the alpha iron crystal and to small crystal size. It appears, however, that the explanation suggested by Nádai is still the best one.

The flow layers obtained under different stress conditions have been observed in the past by various means. One of the most widely used methods is the flaking off of some brittle substance on the surface of the bar, such as mill scale, whitewash, rosin varnish, etc. These methods have the common disadvantage that they do not reveal the entire plastic flow. In addition, they do not show the three-dimensional character of the flow at the surface. Actually the layers either project above or below the surface of the metal. The Fry etching method[10] is valuable in that it enables one to determine the type of flow inside the surface of the metal; as, for example, in a twisted shaft. So far, however, the Fry etching procedure has been limited to mild steels of the proper nitrogen content. Perhaps the most general method from the point of view of applicability to different materials, without the disadvantages of the other procedures mentioned, consists in observing the flow layers on the highly polished surfaces of the metal. However, in order to

properly observe the layers on a highly polished surface, use must be made of suitable optical equipment utilizing reflected light. For this purpose, a few years ago Dr. A. Nádai and the writer designed a special apparatus[11] whose function was the observation of samples that had already been tested. This apparatus was used solely to photograph or observe tested specimens at either natural size or with a small magnification, observations being made on the ground glass of the camera.

This paper describes a new apparatus, recently developed, which considerably extends the field of application of the earlier equipment, and discusses the test results obtained.

The New Plastiscope

In order to reveal the plastic flow that appears on the highly polished surfaces of metal when stressed into the plastic range, a new special optical equipment hereinafter referred to as the Plastiscope was designed, in which a special system of reflected light was used. The new equipment was so constructed that it is now possible to use it for: (1) projection of the image of a tested specimen on a lecture-room screen to large magnification, (2) taking still photographs at small or large magnification, (3) revealing the plastic flow on a test piece *continuously* as it occurs during testing by easily moving the equipment to a testing machine and observing the image in a large ground glass [30 by 50 in.] to considerable magnification and without the necessity of darkening the room, (4) showing the plastic flow *continuously* and in detail in such processes as the rolling of metals, (5) taking *motion pictures* of the plastic flow process *continuously*. As far as the author is aware, no reported attempts have been made to record *in motion* the plastic flow layers as they form on the highly polished surfaces of metals. Although the lens system is fundamentally the same as in the old equipment, the range of usefulness of the apparatus has thus been considerably extended.

Fig. 1 shows the Plastiscope in position at a testing machine, indicating the setup used either to observe the plastic flow taking place or to make motion pictures of it continuously. The testing machine is shown at the extreme right side of the picture with a small rectangular compression-test specimen in place, which is being tested. A large duralumin hood covers part of the still camera in order to exclude stray light and the image of the specimen may be seen on the adjustable ground glass placed near the rear of the hood. The height of the bench is adjustable through wide ranges in order to fit various testing machines for tension or compression tests. A motion picture camera is placed back of the ground glass at the extreme left of the picture. During the tests this camera was focused on the specimen image on the ground glass and continuous records made of the entire flow process from start to finish. Supersensitive

16-mm. panchromatic film was used throughout the tests. The camera speed was 8 frames per second at f 3.5.

Fig. 2 shows a close-up view of the lens system used. This follows somewhat closely the so-called Toepler Schlieren method,[12] which

1

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FIG. 1.—PLASTISCOPE SETUP FOR TAKING MOTION PICTURES OF PLASTIC FLOW IN A COMPRESSION TEST PIECE.
FIG. 2.—CLOSE-UP VIEW OF LENS SYSTEM USED IN FIG. 1.

normally is used in observing the changes in refractive power of transparent bodies such as lenses. The light proceeds from a 500-watt tube lamp through condensers and a water cell for cooling to a right-angled prism, where it is bent nearly parallel to the axis of the still camera. It

then passes through a double convex lens in front of the test specimen, is reflected by the surface of the test piece back through this lens and then into the lens of the still camera, where the image of the specimen is transferred to the ground glass at the rear of the hood. Since this lens system is described elsewhere,[11,12] it will not be discussed further here.

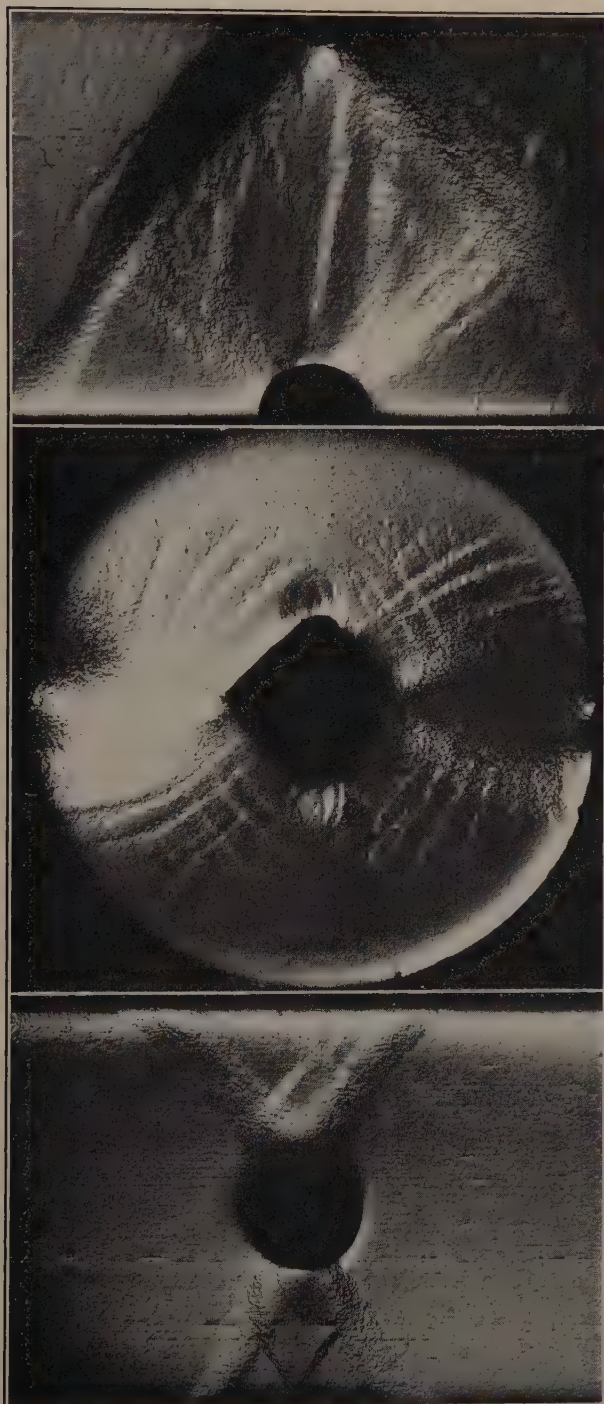
The equipment is also adaptable to the projection of tested specimens on a screen in a darkened lecture room. This may be accomplished merely by sliding the hood off the optical bench, reversing the camera on the horizontal slide-bar, placing an adjusting piece on the test-piece

FIG. 3.—PLASTISCOPE ADAPTED FOR PROJECTION OF TESTED SPECIMENS ON LARGE SCREEN.

support, and tilting the slide-bar to the desired height. The equipment so arranged is shown in Fig. 3. The convex lens in front of the specimen shown on the test-piece support can be rotated or adjusted in all directions to prevent unwanted reflections on the screen. The test-piece support can be rotated about horizontal and vertical axes by means of the small handle and an adjusting screw shown, to obtain the optimum angle of reflection, and can be adjusted in height by rack and pinion drive. The position of the lens (double convex) in front of the test specimen is adjusted so as to turn about a vertical axis as near to the specimen as possible. With the equipment in this position it is also a simple matter to take still photographs of the specimen on the test-piece support.

PLASTIC FLOW IN TENSION AND COMPRESSION

In the tests to be described here SAE 1112 annealed mild steel was used throughout, since this material exhibits clear flow layers upon



(a) (b) (c)

FIG. 4.—PLASTIC FLOW OF MILD STEEL TEST PIECES THAT WERE COMPRESSED VERTICALLY.
a. Cross section $\frac{3}{4}$ by $\frac{5}{8}$ in., hole $\frac{3}{16}$-in. diameter. Load 14,100 lb.
b. 1 in. dia., $\frac{3}{4}$ in. thick, $\frac{3}{16}$-in. square hole. Load 9400 lb.
c. Cross section $\frac{3}{4}$ by $\frac{5}{8}$ in.; grooves $\frac{3}{32}$ in. radius. Load 14,100 lb.

yielding. Fig. 4 shows three photographs made with test pieces of different shapes, each containing a hole or notch in order to provide localized yielding and stressed in compression with the axis of stressing vertical. These photographs were made with the new equipment after the samples in the testing machine were unloaded, and were taken on the still camera of the equipment. The dimensions of the test pieces, together with the final loads, are indicated on the figure. In the circular disk with the central square hole, the diagonal of which is parallel to the axis of stressing, not only is an orthogonal family of flow layers produced near the points of load application, but flow layers have started from the corners in a horizontal plane. In the rectangular test pieces, it is an interesting fact that in both samples horizontal flow layers began to form before the layers that are inclined to the bar axis.

Fig. 5 shows the type of flow layers received for both solid and hollow cylinders compressed laterally. These photographs were enlarged from 16-mm. film taken on the motion picture camera and represent the type of yielding received at an intermediate stage of the testing. Such enlargements from a single frame, however, are seldom as clear as the projected image when the film is shown on a screen. Aside from local distortion at the points of load application for the hollow cylinder, there is a flow layer concentric with the hole. For the solid cylinder, which represents the type of yielding in a roller bearing, it is possible to determine the equation of these flow layers. The principal stress trajectories are a family of bicentric circles, and the shear-stress trajectories cut these circles at 45°. The equation of these flow layers may then be obtained by mapping conformably from a $[u,v]$ plane on to the $[x,y]$ plane by means of the relations

$$x = \frac{a \sin v}{\cosh u - \cos v}$$
$$y = \frac{a \sinh u}{\cosh u - \cos v} \qquad [1]$$

where a is the radius of the cylinder and u and v are related to each other by the equation

$$v = \pm u \pm b$$

where b is an arbitrary constant. The equations (1) are the parametric equations of the shear-stress trajectories, where the origin of the (x,y) coordinates is at the center of the circle of radius a.

Tensile tests were also made on lap-welded bars of SAE 1112. After the bars were arc-welded they were annealed at 900° C. for 1 hr., cooled in the furnace, machined, and then polished. Fig. 6 shows an enlargement from 16-mm. film of two frames at one junction of these bars, indicating the mechanism of yielding at an early stage in the flow process.

Yielding began at the junction of the fillet and the upper bar. A flow layer then appeared through the throat of the weld at a load of 14,000 lb.,

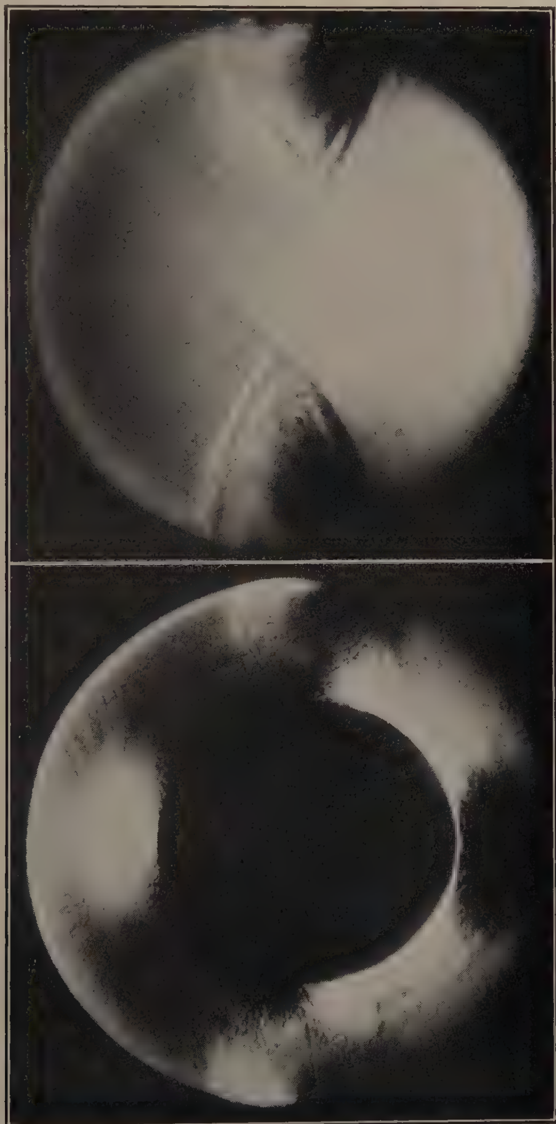


FIG. 5.—ENLARGEMENTS FROM 16-MM. FILM OF PLASTIC FLOW IN SOLID AND HOLLOW CYLINDERS COMPRESSED LATERALLY.

a. Solid cylinder 1-in. dia., ¾ in. thick.
b. Hollow cylinder 1-in. outside diameter, ¾ in. thick, ½-in. inside diameter, ¾ in. thick.

as shown. After this the parent metal began to yield, and final failure took place through the throat of the weld parallel to the flow layer, which

FIG. 6.

FIG. 7.

FIG. 6.—FLOW LAYERS IN AN ARC-WELDED LAP JOINT SHOWING TWO FRAMES ENLARGED FROM MOTION-PICTURE FILM.
Bars ½ by 1$\frac{3}{16}$ in. each. Load 14,000 lb.

FIG. 7.—FLOW LAYERS IN A GAS-WELDED BUTT JOINT SAME ENLARGEMENT AS FIG. 6.
Bars ½ by ⅞ in. each. Load approximately 12,500 lb.

appeared near beginning yielding, at a load of 23,000 lb. The same result was obtained on a similar run with another test bar.

Fig. 7 shows an enlargement of two frames at an intermediate stage in the yielding of a gas-welded butt joint, which was heat-treated after welding in the same manner as for the former test using the same parent metal. In this case, initial yielding began along the side of the double-vee weld, a layer forming at the junction of weld and parent metals; the metal in the weld began then to yield completely and final failure took place at a load of 18,700 lb. through the weld, the line of failure running along the edge of the weld in the same manner as for beginning yielding. Another similar bar tested, which was arc-welded instead of gas-welded, showed similar results at beginning yielding in that two vee layers formed along the junction of weld and parent metal. In the latter, however, the weld metal itself did not then continue to yield but the parent metal below and above yielded first, followed by later yielding through the weld metal. Final fracture in this piece did not occur throughout the weld, but took place above in the parent metal at a load of 27,000 lb. Although it was not a primary purpose of these tests to show the relative strengths of arc-welded and gas-welded joints, the main purpose being to describe the mechanism of yielding, the fracture loads were given to complete the picture.

A small square block of this same material was then compressed between two hardened rectangular punches. Fig. 8 shows an enlargement of two frames from the film, indicating the type of yielding received at an intermediate step in this flow process. These flow layers are similar to those in Fig. 5 for the solid cylinder.

Various other test bars were stressed in compression and in shear and recordings of their mechanisms of yielding were made on the 16-mm. film. These will not be discussed here, since the examples given illustrate the use of the apparatus. They include cylinders with holes of different shapes, rectangular test pieces with grooves or holes, rectangular bars tested in double shear, and square bars compressed diagonally.

Plastic Flow in Cold-rolling

The Plastiscope is readily adaptable to recording on motion picture film the flow layers received during the cold-rolling of metal bars. Fig. 9 shows the apparatus in position adjacent to a small rolling mill at the beginning of such a test. The frame that was used in former tests to hold the double convex lens near the test bar is replaced by another clamped to the stool in this picture. Fig. 10 shows a close-up view of the arrangement. The cover plate on the lower roll was removed in order to place the lens in position. A lens was cut into rectangular shape, to facilitate its insertion between the rolls next to the test bar. In all other

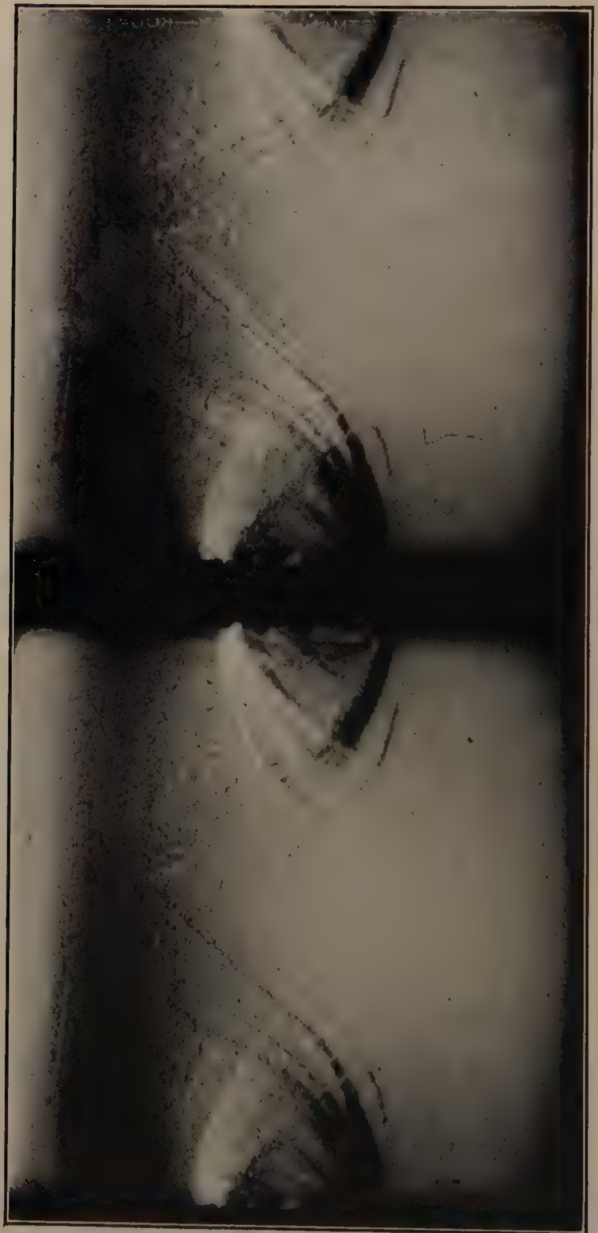


FIG. 8.—SQUARE BLOCK PRESSED BETWEEN TWO HARDENED STAMPS SHOWING FLOW LAYERS ENLARGED FROM FILM.
Blocks 1 in. square, 5/8 in. thick. Stamp 1/4 in. wide.

respects the setup was the same as before. Instead of rolling the bar under power, a large wrench was attached to the square shank on the other side of the rolls and the bars rolled with a small reduction by slowly turning the wrench. The motion picture camera was placed in position back of the ground glass on the apparatus and the mechanism of yielding recorded from the time of entry of the bar into the mill to the time of exit after the entire bar had been rolled. Fig. 11 shows an enlargement from the 16-mm. film of two frames when the bar was about halfway through the rolls. The bar was originally 0.994 in. square and had a highly

Fig. 9.—Plastiscope in position for rolling-mill test.

polished surface along its entire length. The reduction was 2.40 per cent. It is apparent from Fig. 11 that the flow layers in this test form a family of curves closely approximating ordinary cycloids. In other words, comparing Fig. 11 with Fig. 5 for the solid disk, for the rolled bar, as might be expected, the left half of the cylinder of Fig. 5 can be thought of as being extended an infinite distance away from the right half, so that the orthogonal curves supplied by the left half do not appear in the picture of the flow layers in the rolled bar. After tracing the flow layers received in the rolled bar upon the ground glass of the hood and comparing the curves obtained with cycloids, the agreement was found to be very close.

Some time ago L. Prandtl[13] gave the solution for the two-dimensional plastic flow of metals between two rough parallel plates provided flow can proceed in one direction only. In this problem two cases were considered; namely, (1) that in which flow was prevented in one direction and produced in the other by squeezing the plates together, called the passive

case, and (2) that in which flow was produced toward one side by forcing a piston in from the other, tending to separate the plates; called the active case. The first, or the passive case, may be thought of as similar to the rolling problem provided the length of Prandtl's bar undergoing flow is considered to be that portion of the rolled bar between the rolls, and in contact with them. This solution considers a uniformly increasing normal pressure on the bar, which would be maximum near the center

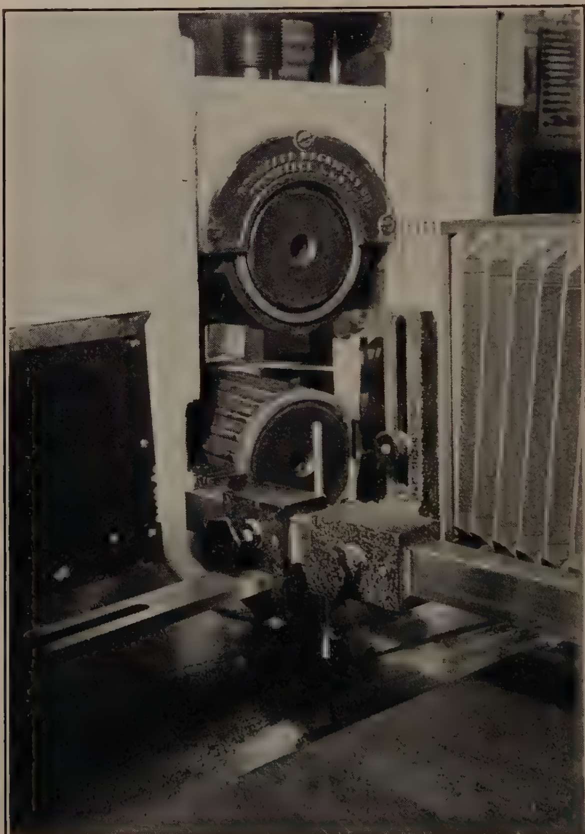


FIG. 10.—CLOSE-UP VIEW OF APPARATUS FOR ROLLING-MILL TEST.

line of the rolls together with uniform shearing stresses on the sides of the strip. In this case the flow layers were cycloids, whose equations are as follows, for one family of slip lines,

$$\begin{aligned} x &= -a[2\beta + \sin 2\beta] + c_1 \\ y &= a \cos 2\beta \end{aligned} \qquad [2]$$

and for the orthogonal family

$$\begin{aligned} x &= a[2\beta - \sin 2\beta] + c_2 \\ y &= a \cos 2\beta \end{aligned} \qquad [3]$$

where $0 < \beta < \frac{\pi}{2}$, a is half the thickness of the bar, c_1 and c_2 are constants, and the origin of coordinates (x,y) is chosen on the center line

FIG. 11.—FLOW LAYERS OBTAINED IN ROLLING-MILL TEST ENLARGED FROM MOTION-PICTURE FILM.

of the bar at the end where the vertical normal pressure is zero, y being in the vertical direction, as shown in Fig. 12. It may be seen that equa-

tions 2 and 3 are merely the equations of cycloids in parametric form, the curves for which may be generated by a point on a circle of radius a when the circle is allowed to move without slip along the edge of the bar. Flow

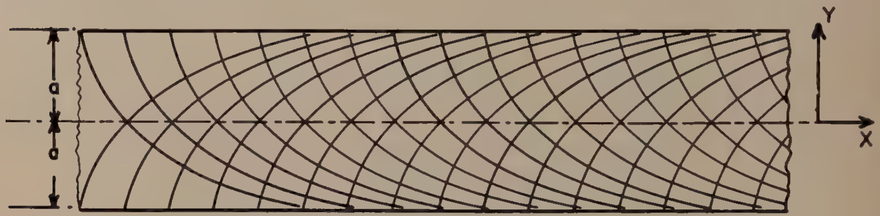


Fig. 12.—Flow layers produced by cold-rolling a mild-steel bar.

layers so generated on Fig. 12 may now be compared with those obtained on a still photograph of the bar taken by the apparatus after rolling as shown in Fig. 13.

This last example is somewhat illustrative of the value of observations of these flow layers, as in such problems it may be possible to work back

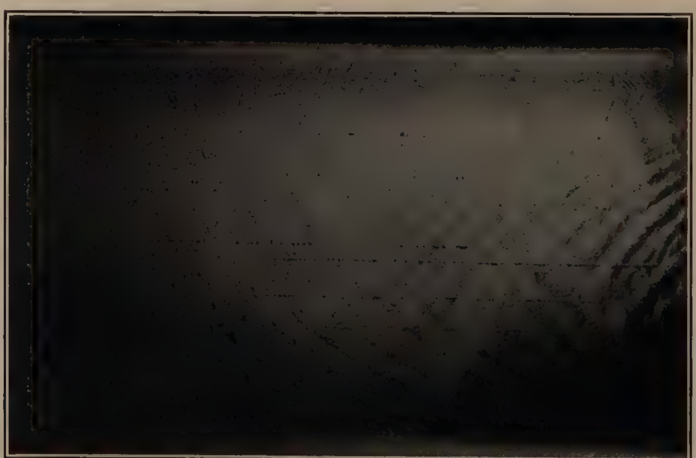


Fig. 13.—Flow layers received in a rolled bar of mild steel.

fram such experiments to the stress distributions which otherwise might be very difficult to determine.

Summary

In order to reveal plastic flow in the form of Lüder's lines which appear on the highly polished surfaces of mild steel when stressed above the yield point, a new special optical bench has been designed using a system of reflected light. This optical bench differs from the one designed some time ago by A. Nádai and the author, in that although the

lens system is fundamentally the same the range of usefulness has been considerably extended. The equipment is so designed that it is possible now to use it for: (1) projection of the image of tested specimens on a class or lecture room screen to a large magnification, (2) taking still photographs at small or large magnification, (3) revealing the plastic flow on a test piece continuously as it occurs during testing by easily moving the equipment to a testing machine and observing the image in a large ground glass to considerable magnification, (4) showing the plastic flow in such processes as the rolling of metals, (5) taking motion pictures of the plastic flow process continuously, etc.

As far as the author is aware, no reported attempts have been made to record in motion the plastic flow layers as they form on the highly polished surfaces of metals. With this in view, motion pictures were made of the yielding in test pieces stressed in compression in the form of disks with or without holes, rectangular bars with and without holes, and rectangular bars with notches. Further, films were made recording the mechanism of yielding in both butt and lap welds, bars undergoing double shear, and in a bar as it passes between the rolls in the rolling mill, which concludes the film. From the observation of the mechanism of plastic flow in the various cases mentioned it was possible to show how metal yields near welds, in bars during cold-rolling, etc.

Acknowledgment

The author wishes to express his appreciation for the interest in and support given to this investigation by various members of the Faculty at the Massachusetts Institute of Technology, particularly to Prof. J. C. Hunsaker, Prof. C. E. Fuller, and Prof. J. M. Lessells. He also desires to acknowledge the assistance of F. H. Conant and P. R. Shepler in making the tests and the careful construction of the apparatus and test pieces by F. W. Perkins and H. Johnson.

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DISCUSSION

(*M. Gensamer presiding*)

A. Nadai,* East Pittsburgh, Pa. (written discussion).—The study of the flow layers occurring in mild steel, and more generally of the regular shapes of the surfaces of slip that appear on test pieces of certain polycrystalline ductile metals under special conditions and under varying stress, besides being a most charming subject in itself for all those interested in the mechanisms of the flow of the ductile metals, has revealed considerable instructive information about the true nature of the plastic flow of solids. Since the French engineer, Hartmann, 45 years ago published the first monograph devoted exclusively to the observations of the flow figures appearing on the surface of mild-steel specimens, and since Otto Mohr utilized similar observations for developing the theory of strength and of rupture, the laws of the formation of these flow layers have been studied by A. Fry, C. W. MacGregor, C. Elam, E. W. Fell, K. Yuasa, F. Körber, E. Siebel and others. However, as the author states, the mechanical conditions for the formation of these slip layers are still far from being satisfactorily understood and it is therefore to be commended that new equipment for their observation in an improved form has been developed by the author. For example, under a state of pure tension the layers should form in planes inclined at an angle of 45° to the axis of the bar. In flat bars, however, it is noticeable that the only layers that usually form are those that are perpendicular to the flat sides. The writer showed, at the International Congress for Testing of Materials in April 1937, in London, motion pictures of the formation of these lines in a series of tensile tests made with flat bars and with plates subjected to bending by concentrated forces. The influence of small notches upon the formation of the thin slip layers is very pronounced. Note the long fine lines appearing in Fig. 14 and their interruption when the test bar has a number of small notches as shown on the left edge of specimen No. 294 reproduced in Fig. 15. In torsion of round bars it has been observed that usually a radial system of lines (flow layers) appear in the etchings of the cross sections, which are perpendicular to the axis of the round bar, and that these lines are approximately equidistant.

These and similar observations seem to indicate that the formation of the lines among other things depends on the conditions of support in the heads of a test bar. More precisely, the degrees of freedom in the heads of a specimen have an influence on the mode in which the Lüders' lines will appear. Similarly, small notches (Fig. 15) have an influence, as Dr. MacGregor has also shown in a former investigation. One of the most puzzling phenomena is the regularity of the distance at which one line forms after the other. Evidently an oscillating movement of extreme smallness is building up a slight increase of stress until one line begins to form. After it has run across the width of the flat bar, apparently a period of stress relief follows, which interrupts the process until the stress has increased again for formation of the next layer. This can be corroborated by observations of continuous stress-strain curves.

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* Research Laboratories, Westinghouse Electric and Manufacturing Co.

FIG. 14.—SLIP LINES ON FLAT BAR OF STEEL.

FIG. 15.—FLOW LINES ON FLAT BAR HAVING SMALL NOTCHES.

A number of other influences, particularly the effect of the speed of stretching, has been brought out by E. A. Davis recently.[14]

C. W. MacGregor (written discussion).—The photographs showing plastic flow in whitewashed tensile-test pieces which Dr. Nadai included in his discussion are indeed interesting and show a very large number of slip lines. When small notches

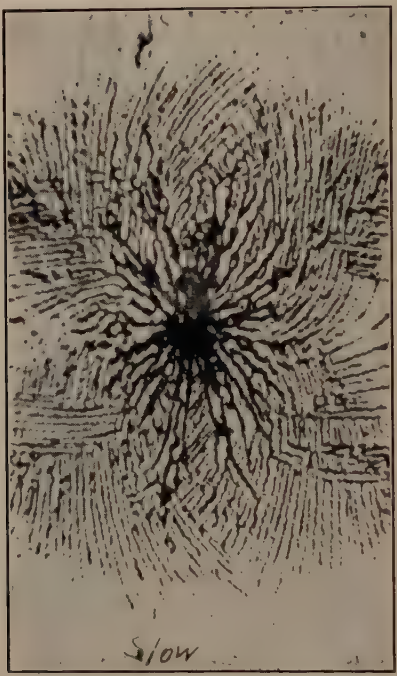

Fig. 16.—Flow lines on rectangular plate after bending through a concentrated load

are produced in the sides of the test pieces, it appears that flow layers usually proceed in a direction perpendicular to the axis of the bar instead of along 45° planes. The whitewash method seems to be extremely useful, especially for cases such as shown in Fig. 16. The author found it difficult to photograph on a polished surface such a case, since a special type of illumination is necessary.

[14] E. A. Davis: Effect of the Speed of Stretching and the Rate of Loading on the Yielding of Mild Steel. *Jnl. Applied Mechanics* (Dec. 1938).

Microhardness of Bearing Alloys

By L. L. Swift*

(Detroit Meeting, October, 1938)

At the present time there are four base metals being used for automotive bearing alloys. Of course there are numerous variations in the amounts of alloying elements added to each base metal and nearly all of these alloys have the conventional, if not classical, duplex structure; that is, they are composed of a hard constituent embedded in a soft matrix. The well-known theory is that the former will wear well, while the latter will be plastic enough to allow the bearing to be broken in and conform to the contours of the shaft.

The requirements of the modern bearing have been most aptly described by W. M. Corse:

> In order to meet the engineering demands of today a good bearing metal must be able to carry the weight of the shaft and stand up under steady or suddenly applied loads, or even blows in some types of service. A certain amount of plasticity is desired to compensate for minute irregularities in the shaft or bearing surface, and to permit yielding, thereby avoiding dangerous stresses in bearing and shaft and preventing overheating and rapid wear of parts. Less plasticity is required in a bearing metal if the surfaces of bearings and journals are machined accurately, aligned, and kept in alignment. It is desirable, of course, that a bearing metal have a low coefficient of friction. Under most operating conditions the friction depends on the unit pressure of the bearing, the speed, the temperature, and the properties of the lubricant.
>
> A good bearing metal must have a low rate of wear to reduce the necessity for frequent replacements, and adjustment of the bearings. It must wear more rapidly, however, than the journal or shaft running on it, because replacement of the journal or shaft is more difficult and costly than replacement of the bearing.[1]

The hardness of the bearing alloy is a property closely related to several of the foregoing. With a duplex microstructure, the measurement of hardness with any of the usual commercial devices means little. The Bierbaum method of measuring the hardness of the individual constituents was developed to fill this need.

Microcharacter

The Bierbaum Microcharacter[2,3] measures the scratch-hardness of a solid by pulling a weighted diamond point over the surface. The diamond point is ground so that it is the corner of a cube, and mounted

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* Control Metallurgist, The Cleveland Graphite Bronze Co., Cleveland, Ohio.

[1] References are at the end of the paper.

with the cube diagonal in a vertical position. One edge of the cube and the corner forms the cutting edge and the diamond is fastened to a flexible stylus. Since the width of the scratch will vary inversely with the hardness, Bierbaum developed the following formula:

$$\text{Microhardness} = K = \lambda^{-2} \times 10{,}000$$

where λ is the width of the scratch in microns.

Bierbaum and others[4,5] have pointed out that it is optically impossible to measure the distance A across the microcut, as shown in Fig. 1. The usual procedure is to measure the distance B, which will be the total width of metal displaced. The observer must use his own judgment in choosing portions of the microcut where B can be accurately measured. He will attempt to avoid measuring at points where a burr obscures the actual width of displaced metal, as shown by C in Fig. 1.

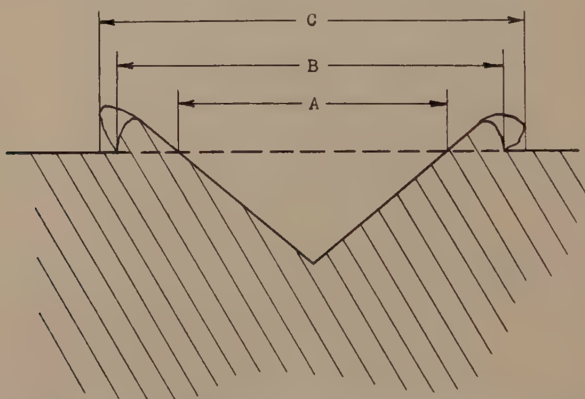

FIG. 1.—DIAGRAMMATIC SECTION THROUGH MICROCUT. AFTER BIERBAUM.

Williams[5] has pointed out that the behavior of various substances when scratched will be important in using the microcharacter. He draws a most apt comparison between the furrowing of putty with a knife and the scratching of a glass rod with a file. The putty is displaced but it is so plastic that a new outer surface is formed and none of the putty is actually severed from the parent mass, whereas pieces of the brittle glass are broken away, and we can suppose that the scratch-width would actually be that of A in Fig. 1.

The writer measured the microhardness of three intermediate phases, as will be noted later. Each one showed some tendency to splinter, but no difficulty was encountered in finding suitable portions of the microcut for measurement.

As the diamond point "ploughs" across the test surface, plastic deformation and also work-hardening takes place. The latter is most noticeable in the displaced metal on each side of the scratch. In measuring the width of the scratches in different alloys, the ratio between the

total width of the scratch and the displaced metal on either side ($B/(B - A)$ in Fig. 1) seemed to vary considerably. Before the displaced metal was pushed aside, it was first piled up in front of the diamond point. Thus the final result (scratch width) will be a measure of (1) the plasticity of the unworked metal below the surface of the test piece and (2) the resistance to further deformation of the displaced and work-hardened metal. Would the accurate measurement of the ratio mentioned above provide a way of determining the ability of a metal to be work-hardened?

The following procedure after the scratch was made was adopted as standard:

1. The piece was swabbed with xylol to remove the watch oil used in lubricating the diamond point, and then swabbed with ether.

2. The width of the scratch was measured on a Leitz Micro-Metallograph, using a 5.5-mm. objective and a Filar micrometer having a 20× eyepiece. This gave a magnification of 900. Before the measurements were made, this optical combination was calibrated.

Some workers who have used the microcharacter recommend rubbing the microcut with elder pith to remove burrs. The writer found no difference in the widths of microcuts that had been rubbed with elder pith and others that had not been so treated.

TABLE 1.—*Microhardness of Specimens*

Material	High		Low		Difference		Average	
	λ	K	λ	K	λ	K	λ	K
Tin-base babbitt:								
Straits tin	32.20	9.6	33.40	9.0	1.20	0.6	32.76	9.3
Matrix	23.79	17.7	25.34	15.6	1.55	2.1	24.44	16.7
Cu-Sn crystals	3.66	745.1	4.18	572.1	0.52	173.0	3.96	636.0
Lead-base babbitt:								
Lead	51.72	3.7	53.62	3.5	1.90	0.2	52.84	3.6
Matrix	32.80	9.3	34.39	8.5	1.59	0.8	33.62	8.9
Sb-Sn crystals	6.03	274.7	6.77	218.4	0.74	56.3	6.38	245.8
Cadmium-base babbitts:								
Cadmium	26.51	14.2	27.50	13.2	0.99	1.0	26.85	13.9
Matrix, Cd-Ni babbitt	22.58	19.6	25.04	16.0	2.46	3.6	23.19	18.6
$NiCd_7$ crystals, Cd-Ni babbitt	5.26	361.7	6.08	270.8	0.82	90.9	5.64	313.7
Cd-Ag-Cu babbitt	17.24	33.6	20.13	24.7	2.89	8.9	18.53	29.1
Copper-lead alloy:								
Copper	10.04	99.2	14.61	46.8	4.57	52.4	12.69	62.0
Copper in copper-lead alloy	10.26	95.0	15.26	43.0	5.00	52.0	13.32	56.4
Lead in copper-lead alloy	35.26	8.1	38.00	6.9	2.74	1.2	36.51	7.5

In Table 1 is recorded under "High" the highest single reading of each constituent, and under "Low" the reading giving the smallest microhardness number; under "Difference" the difference between the high and low

reading, or range in microhardness of the constituent. The results under "Average" are the average of all readings.

Tests and Results

Tin-base Babbitt.—The specimen used contained 7.5 per cent Sb, 3.25 per cent Cu and balance Sn. The matrix of this alloy is composed

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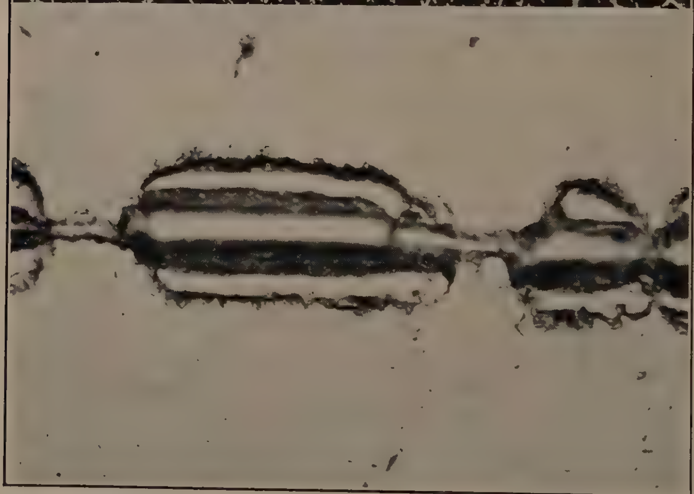
3 

Fig. 2.—Structure of tin-base babbitt. × 100. Etch, $FeCl_3$.
Fig. 3.—Microcut in tin-base babbitt. × 750. Unetched.

of the alpha solid solution of antimony in tin, plus a pseudo-eutectic.[6] The hard constituent, however, is confined entirely to copper-tin needles. Because of casting conditions no antimony-tin cubes are present. Fig. 2 shows the typical structure of this alloy.

The effect of adding antimony to tin, the base metal, is apparent when comparing the results in Table 1. The scratch-width shows a decrease of 8.32 microns, or about 25 per cent, while the microhardness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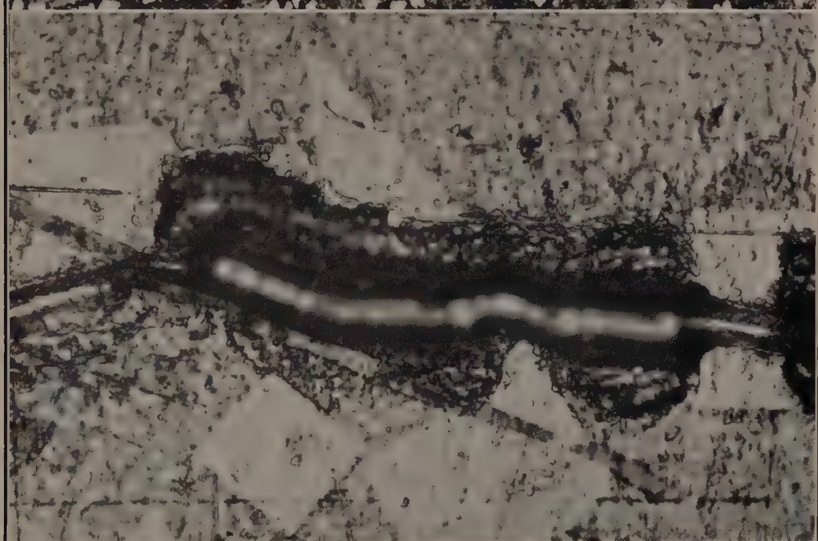
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Fig. 4.—Structure of lead-base babbitt. Fast-cooled. × 500. Etch, HCl.
Fig. 5.—Microcut in lead-base babbitt. Slow-cooled. × 750. Unetched.

increases from 9.3 to 16.7. The way in which the width of the scratch varies as it crosses the copper-tin needles is shown in Fig. 3.

Lead-base Babbitt.—This alloy contains 10 per cent Sn, 15 per cent Sb, 0.5 per cent Cu and balance lead. This composition is within the limits of the specifications for SAE No. 14 lead-base babbitt.

The primary phase to crystallize during the process of solidification is probably the compound Cu_2Sb, which appears as purple needles. One is shown in Fig. 5. The secondary phase is the hard constituent, i.e.

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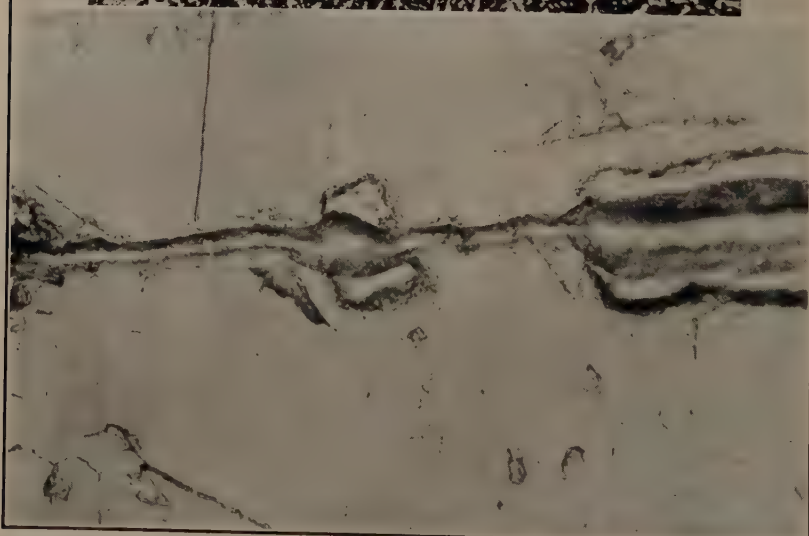

Fig. 6.—Structure of cadmium-nickel babbitt. × 100. Etch, $FeCl_3$ + alcohol.

Fig. 7.—Microcut in cadmium-nickel babbitt. × 750. Unetched.

the familiar antimony-tin cubes. Their distribution in the matrix is apparent in Fig. 4.

According to Weaver,[7] the matrix contains a pseudo-eutectic of beta (mainly SbSn) plus delta (a lead-rich solid solution) and also a ternary

eutectic of alpha plus beta plus delta phases. The alpha phase is an antimony-rich solid solution.

A comparison of the results in Table 1 shows that the addition of antimony and tin to the lead hardened it considerably, since the scratch-width decreased about 36 per cent and the microhardness was more than doubled. The heterogeneity of the matrix is apparent in Fig. 5. Note that the displaced metal on each side of the microcut appears as a mass of dissimilar particles, many of them appearing light in color.

Cadmium-nickel Babbitt.—This is a binary alloy, and contains 1.25 per cent Ni. According to the most recent investigation of this system,[8] the eutectic between cadmium and the intermediate phase ($NiCd_7$) contains 0.25 per cent Ni. The alloy of this composition thus contains 14.95 per cent $NiCd_7$ as "hard constituent." The remaining eutectic forms the matrix, and contains 3.60 per cent $NiCd_7$. The structure of this babbitt is shown in Fig. 6. The white crystals are the primary dendrites composed of the cadmium-nickel intermediate phase.

A comparison of the results in Table 1 shows that the addition of nickel to cadmium caused a decrease in scratch-width of 3.66 microns, or about 13.5 per cent. The microhardness was raised from 13.9 to 18.6, while the matrix of this babbitt is slightly harder than that of the tin-base babbitt.

The larger variation in the measurements of scratch-width of the matrix (2.46 microns) is probably because the cadmium-nickel eutectic is lamellar. Portions of the scratch running across a series of eutectic plates would have a narrower scratch-width and would appear harder than the portions in which the scratch runs parallel to a series of eutectic plates. The typical appearance of the microcut is shown in Fig. 7.

Cadmium-silver-copper Babbitt.—The sample used for this work contained 0.72 per cent Ag, 0.5 per cent Cu and balance Cd, and had been annealed for 100 hr. at 300° F. According to Smart,[9] this alloy consists of cadmium-silver solid solution and a eutectic of Cd-$CuCd_3$. The structure and appearance of the microcut are both shown in Fig. 8.

This alloy does not possess the conventional duplex structure, at least not in the usually accepted sense of the term. It will be noted in Table 1 that the variation in microhardness is greater than in any of the matrices of the preceding bearing alloys that were tested, but this variation is still less than the difference between any of the matrices and the intermediate phases.

However, one of the phases present in the eutectic is an intermediate phase, and thus one would expect the eutectic areas to be harder than the cadmium-silver solid solution. The writer made a series of measurements on both the light, solid-solution areas and on the darker portions containing the eutectic. The results are recorded in Table 2. Considering the limitations of the microcharacter and optical equipment

used, these results indicate that there is no difference in hardness between these two areas.

TABLE 2.—*Microhardness of Constituents of Cd-Ag-Cu Babbitt*

	λ	K
Light areas: Cd-Ag solid solution	18.47	29.3
Dark areas: Cd-$CuCd_3$ eutectic	18.58	29.0
Difference	0.11	0.3

Copper-lead Alloy.—Before the microhardness of this alloy was measured, measurements were made of the microhardness of an unetched

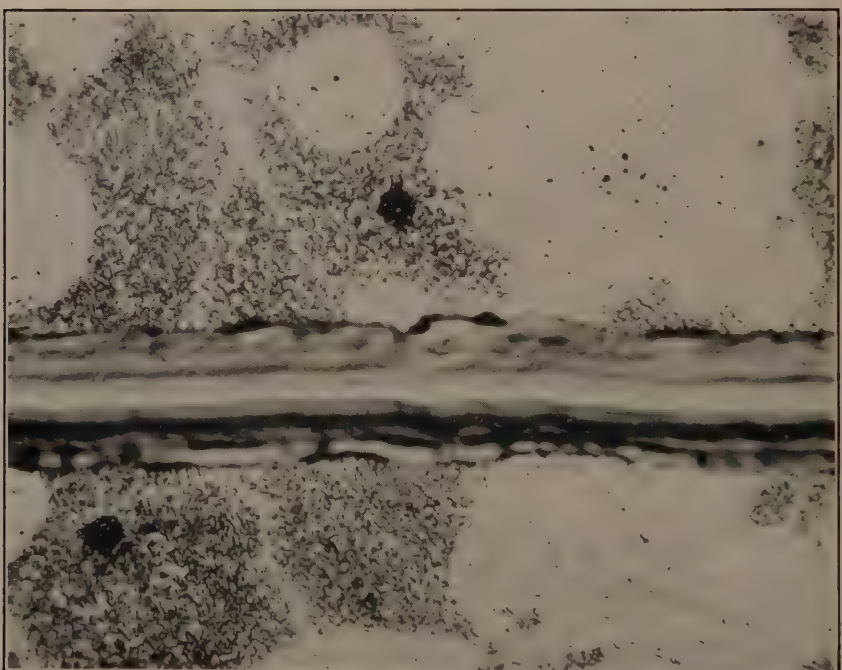

FIG. 8.—CADMIUM-SILVER-COPPER BABBITT SHOWING STRUCTURE AND MICROCUT. × 1000. ETCH, $FeCl_3$ + ALCOHOL.

piece of pure sheet copper that had been annealed for 29 hr. at 750° F. The results showed considerable variation and so the specimen was etched; new microcuts were made and their widths measured. Practically the same variation in hardness was noted in both cases, and the change in width of the microcut as it passed from one grain to another was marked. Fig. 9 shows such a variation. At *A* the microhardness is 96.7, while at *B* it is 48.3.

Conley, Conley, King and Unger,[4] give the microhardness of copper as 74–115 but do not specify whether this is due to cold-work or the

inherent anisotropy of the metal. Williams[5] is more specific. He shows a microcut passing from one grain of copper into another and says:

FIG. 9.—MICROCUT IN ETCHED COPPER. × 750. ETCHED $NH_4OH + H_2O$.

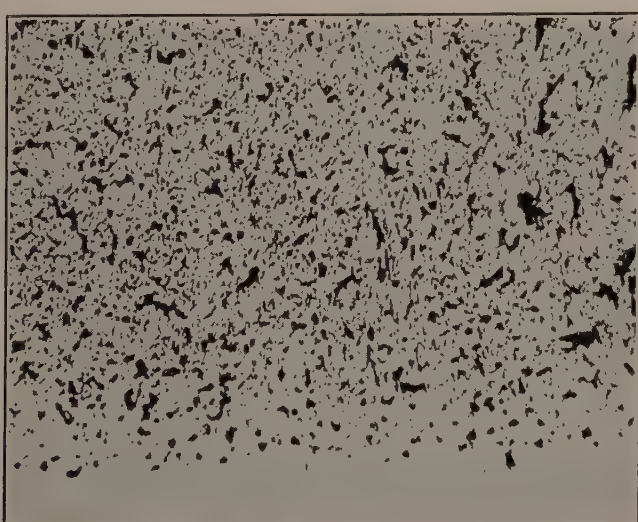

FIG. 10.—STRUCTURE OF COPPER-LEAD ALLOY AS CAST ON STEEL STRIP. × 100, UNETCHED. WHITE STRIP AT BOTTOM IS STEEL BACK.

"Microcut across the surface of a chemically pure piece of copper, showing the anisotropy of copper."

The copper lead that was tested contained approximately 60 per cent Cu and 40 per cent Pb. According to Claus, the eutectic of copper and lead contains 0.06 per cent copper.[10] The specimen tested was cast by pouring the liquid alloy in a thin layer on a moving steel strip. The microstructure is shown in Fig. 10, in the unetched condition. The dark areas are globules of lead trapped in the copper matrix. There is a great variation in size and distribution of these lead globules. Owing to the sudden cooling of the alloy, by sprays hitting the under side of the steel backing, there is also a marked orientation of the mixture, since the copper crystals show a tendency to grow perpendicular to this surface.

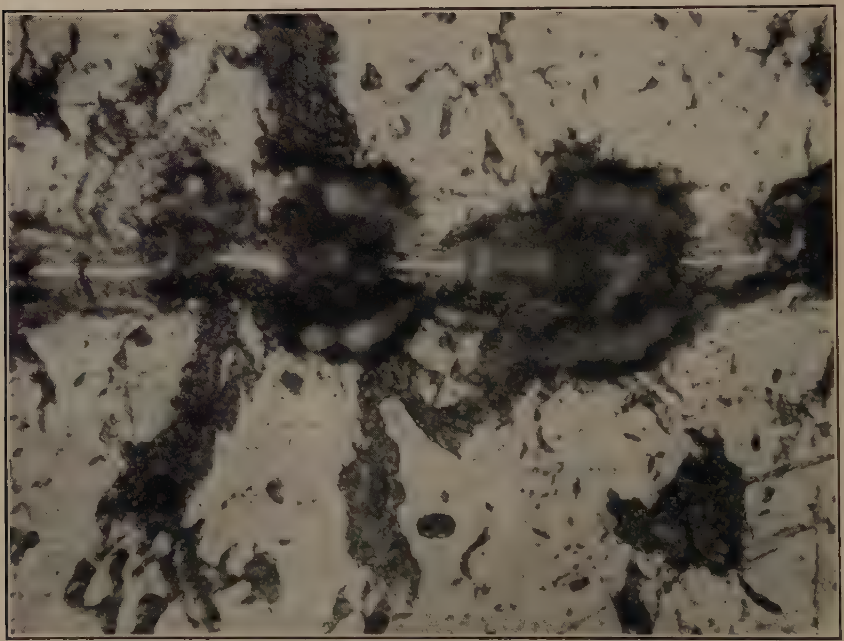

FIG. 11.—MICROCUT IN COPPER-LEAD ALLOY. × 750, UNETCHED.

This alloy differs from the preceding bearing metals. In this, the "hard constituent" is the matrix and is in excess, while the softer, more plastic metal is in the minority. This definitely affected the performance of the diamond point. In passing from a soft metal to a hard one, the scratch-width is reduced at once. But when the diamond traverses a relatively narrow soft area between harder areas, the displaced metal often is pushed out over the hard metal. As a result, areas on the scratch suitable for measurement were not plentiful. Fig. 11 shows the appearance of the scratch as it passes through both copper and lead.

The hardness of the copper in copper lead also showed a wide variation (Table 1). If not due to anisotropy, as mentioned previously, this may be due to extremely small particles of lead, some of which may even be

submicroscopic. The great variation in size of lead segregations is clearly shown in Fig. 11.

It is also possible that the lead may contain minute particles of copper, which would explain the marked difference between the hardness of pure lead and the lead in the copper-lead alloy.

Discussion and Conclusions

The curve showing the relationship between the width of the microcut and the microhardness number is logarithmic. Consequently, variations in the measurement of a wide scratch in a soft metal are not prominent when the measurements are converted to microhardness. The exact opposite is true when measuring a hard substance. This is evident in Table 1. A variation of 0.52 microns in the width of the microcut in the copper-tin crystals resulted in a difference of 173 in microhardness. At the other extreme, in measuring the microcut in lead, a variation of 1.90 microns gave a difference of 0.2 in microhardness.

It is reasonable to expect greater variations in the measurement of a wide scratch in a soft, plastic metal. This variation could be minimized by measuring scratch-width at a lower magnification. But if this were done it is possible that the observer would not be able to pick suitable places on the scratch for measurements with the same ease as at a higher magnification, and would thus lower the accuracy of his results.

Of course, some of this variation in the hardness of the matrices is inherent in these alloys, since the matrices of the first three alloys are all heterogeneous.

In all probability, the variations in the hardnesses of the intermediate phases, as listed in Table 1, may be due to the limitations of the micro-character, the optical equipment and the observer. Conley, Conley, King and Unger[4] point out that "the practical limit of magnification as well as the quality of Filar micrometers make measurements to fractions of microns doubtful." However, the writer recorded the decimal parts of microns in Table 1 in order to show the relationship between the recorded number of micrometer turns and microns in a series of readings on alloys with widely different microhardnesses. None of the writers that have published microhardness results have done this, but have recorded an average obtained from a number of readings.

Incidentally, it is a generally recognized fact that measurements of microhardness made on different machines will not check each other, nor will those of different observers made on the same machine.[11]

The comparison of the microhardnesses of the various bearing alloys with their values as bearing alloys can only be general. The hardnesses of the matrices give us a general idea of the plasticity of the alloys, and if this be true, the lead-base is the most plastic, while the tin-base and cadmium-nickel are about the same.

The compressive strength of the babbitt is important but this property is influenced also by the structure of the hard constituent. The dendritic network in the cadmium-nickel babbitt and the stars and needles in the tin-base babbitt could both be expected to bear part of the load in compression. But one would not expect the antimony-tin cubes to make the lead-base babbitt stronger in compression.

The relationship between the hardness of the crystals in a babbitt and the crankshaft is also of some importance. The copper-tin crystals are generally considered harder than a steel crankshaft and have been known to scratch it. When the writer's average hardness of 636 is compared with a recorded hardness of 297 for ferrite and 600 for pearlite[4] this seems reasonable, even though these results were obtained by different workers.

The relationship between hardness and wear is indefinite. It is claimed that the copper-lead alloys cause excessive wear of the crankshaft, although the copper matrix of copper-lead alloy is not nearly as hard as the intermediate phases present in other bearing alloys.

Coefficient of friction and ability to maintain an oil film are two other properties that may be correlated with the microhardness of a bearing metal, but the exact relationship is indefinite.

While the relationship between the microhardness and the other physical properties of a bearing alloy may be rather obscure at present, there is little doubt that the microhardness test could well be added to the other physical tests usually applied to such metals.

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DISCUSSION

(*John L. Christie presiding*)

C. H. Bierbaum,* Buffalo, N. Y. (written discussion).—The early history of the Microcharacter was beset by many difficulties. After trying various jewels, steels and extremely hard metals, it seemed that the artificial Leuco sapphire would be the most satisfactory material for the cutting point,[12] although it was early realized that the diamond would be the ideal. The incentive for the work was the desirability of determining the relative hardness of the microscopic constituents of the various recognized bearing alloys. A long series of experiments was undertaken before the shape or the form of the cutting point was determined upon, and also the fact that led to the conclusion that a continuous cut was necessary, rather than a scratch.

The difficulty with the artificial sapphire was that many materials are as hard or harder than the sapphire itself—for instance, manganese, fused tin oxide, zirconium and titanium nitrides—also, the fact that all aluminum surfaces are covered with a molecular layer of Al_2O_3, the same substance as the sapphire, causing a distinct wearing or polishing effect upon this jewel, together with the fact that breaking and chipping off of the sapphire point was frequent. All these difficulties could only lead to many discrepancies by different observers, because they were using jewel points that had been subjected to varying degrees of destruction.

The work originally was undertaken by the Bearing Metals Research Committee of the American Society of Mechanical Engineers. Their troubles were fully discussed with Dr. Brashear, president of the Society, who referred the writer to Dr. Kunz, of Tiffany & Co., through whose kindness a list was obtained of both American and foreign lapidaries that were reputedly supplying diamonds for scientific purposes. A long and tedious correspondence resulted, which finally led to the evident conclusion that none of these lapidaries had even the remotest conception of how a sharp point might appear under the microscope.

After several more years of agitation, a favorable introduction was obtained to the work done by F. F. Gilmore, of Boston, who in the first interview said: "I know your problem and have sometimes thought that I would like to try my hand." He did, and in March 1929 his first diamond was submitted, which upon examination under a magnification of 2000 diameters proved to be of a very high order. The facets were true planes, their intersections were straight lines, the point was absolutely sharp and the angle of each facet at the point was 89°, 57″, thus proving the possibility that a diamond could be ground to the specifications laid down, although numerous lapidaries stated positively that beyond the question of a doubt, from their years of experience, no such jewel point could be ground. Diamonds with the accuracy mentioned above have been used in all instruments since July 1930, and every diamond so far supplied has had the personal examination and certificate of accuracy of the writer.

The author says: "Incidentally, it is a generally recognized fact that measurements of microhardness made on different machines will not check each other." This is not an accurate quotation, if intended to be taken from the A.S.T.M. report. Secondly, all of the work done and all of the reports of the A.S.T.M. were at a time prior to the introduction of the diamond as the cutting jewel. These tests were, therefore, made with sapphire points having varying degrees of imperfection. Thirdly, the first instrument made by Zeiss was made under definite specifications and the

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* Vice President and Consulting Engineer, Lumen Bearing Co.

[12] Progress Report of Research Sub-Committee on Bearing Metals. *Trans. Amer. Soc. Mech. Engrs.* (1920) 1099.

writer tested this in comparison with the Spencer Lens Company's standard instrument. Making parallel cuts on surfaces of various metals, cuts made in the same direction and only a fraction of a thousandths of an inch apart, all proved to be absolutely identical. For the foregoing reasons and additional facts that might be stated, justification for this broad criticism of the instrument does not obtain.

The variation in readings as made by different individuals is a fact and this is largely due to inexperience and the confusion arising from not excluding the distorted metal fringe, which usually borders the side of the cut. The author states that wiping with elder pith the surface of the test specimen after the cut is made did not reduce the width of microcut. Such wiping is intended only to eliminate the loose excess fringe.

Another source of confusion often exists where the instrument is used for determining the composite hardness of a heterogeneous alloy having microscopic formations of different degrees of hardness. This is obviously a misuse of the instrument, where Brinell and other standard methods should be used. The object and purpose of the Microcharacter is that of determining the hardness of single crystals, grains or the surfaces of absolutely homogeneous material.

The term "hardness" expresses five distinct ideas, according to Hofman,[13] among which he distinguishes between scratch and cutting hardness. The writer has frequently criticized the use of the term "scratch hardness" when applied to microhardness tests, for the reason that in this test the normal pressure to the test surface must always be greater than the horizontal pull, thus making a continuous indentation or cut. Whereas, if the shape of the point is such that the horizontal pull is as great or greater than the normal pressure, a scratch is the result.

In expressing the results of a hardness test, it is absolutely necessary that the exact manner and details of such a test be given or understood, otherwise the results are meaningless. With this in view, and to avoid unnecessary ambiguity and confusion, the writer has coined the terms: Microcharacter, microhardness and microcut.

In some cases the instrument has been placed in the hands of inexperienced and untrained investigators, which could only lead to unsatisfactory results, and for this reason the writer has given this general precaution: "The investigators should possess the skill and manual dexterity of an accomplished microscopist or that of an experienced physicist" (ref. 3).

The subject of microhardness tests on work-hardened metals has been discussed pro and con by various observers. A careful study and understanding of this subject can be had by slightly etching the test surfaces just enough to bring out the individual grains. It will then be found that the particular grains in which there is no slippage seem to retain their original property, whereas in grains in which distinct slippage has occurred and where a distinct stress exists in such grains work-hardening is distinctly shown. The direction of microcut with reference to the slippage plane again has its effect. Broadly speaking, therefore, the criticism that the Microcharacter does not show an effect of work-hardening on metals is based upon incomplete and inaccurate observations.

It is generally appreciated in making Brinell or similar tests that a time interval must be allowed for the plastic flow of the metal. This same consideration should be given in making microhardness tests, in not moving the cutting point too fast. A safe limit of cutting speed seems to be that of one revolution of the feed screw per second, which has proved satisfactory on pure lead. However, the writer's early caution should always be observed: "The rate of travel should be so slow that no additional indentation is effected by stopping."[12] In the A.S.T.M. Report for 1926,

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[13] Hofman: General Metallurgy, 9. New York, 1913. McGraw-Hill Book Co.

pages 572–573, results are given of the indicated microhardness corresponding to different rates of cutting. Similar results are reported by Hodge.

The author in giving his results gives "high," "low," "difference" and "average." This is commendable. It gives the fullest and most complete information of the test. This the writer appreciates should have been done in his earlier published results, where he has confined himself entirely to averages only (ref. 2).

The author points out the interesting fact that the copper-tin-bearing crystals are harder than the different phases found in soft steel. This is the secret of many vexations that have long been experienced when fitting and starting up copper-tin bronze bearings with soft cold-rolled steel. The results of the author's test on the cadmium-silver-copper babbitt quite agree with those of the writer: "This alloy does not possess the conventional duplex structure," to which the writer would add that for that reason it is distinctly not a bearing metal.

W. J. Conley,* Rochester, N. Y. (written discussion).—Mr. Swift's paper has raised several questions, which can be partly answered by data that have accumulated through work by graduate students in the engineering department of the University of Rochester. In one paper,[14] the microhardness of copper was given as varying from 74 to 115. Part of this variation is due to the difference in purity of individual samples, but a considerable spread is found in the same specimen. This was definitely found to be a result of anisotropy by noting the relation of cut width to the orientation of the different grains as indicated on the etched surface. Effects of this kind must be considered in interpreting Microcharacter readings, especially for constituents such as lamellar eutectics and eutectoids.

In the paper referred to above,[14] it was stated, as Mr. Swift has quoted, that "the practical limit of magnification as well as the quality of Filar micrometers make measurements to fractions of microns doubtful." This statement was made as a warning and to draw attention to the fact that fine equipment is necessary for accurate Microcharacter results. The experience of the writer indicates that careful workers properly instructed in the use of good equipment can duplicate results to tenths of a micron. Usually the results have been recorded in hundredths, but in the final computation of the average and the reported microhardness of a constituent the hundredth has been omitted. It is unfortunate that in an investigation such as Mr. Swift has reported all data cannot be given, but this is usually impossible because of limitation of space. Mr. Swift shows that the Microcharacter is an excellent tool for investigations of individual hardness of microconstituents. However, the following data are submitted to support Mr. Swift's work and to attempt to dispel any misconceptions that may have arisen from the report of the Subcommittee V on microhardness, published in 1926 by the A.S.T.M. (vol. 26, pp. 572–580). This report states that different workers using separate instruments or different observers using the same instrument did not duplicate readings on the same materials with desirable accuracy. The instruments used at that time were an early development equipped with an artificial sapphire, whereas the present ones use the diamond. The sapphire was relatively easily dulled or broken, which brings up a fact that cannot be emphasized too much—namely, that periodic checking of the diamond must be made, to guard against its use with a broken point. With care, this happens rather infrequently, as shown by the use of the instrument available to the writer, which has been used with the same diamond for about seven years. During this period at least 10 dif-

* Professor of Applied Mechanics, University of Rochester.

[14] Conley, Conley, King and Unger: The Microcharacter as a Research Tool. Trans. Amer. Soc. Metals (1936) **24**, 721.

ferent persons have worked with this apparatus, many of whom received their initial instruction on this Microcharacter.

Mr. Swift reports a reading of 636 for pearlite. The corresponding readings obtained in the writer's laboratory are 260 to 2160, average 600, for an 0.8 per cent carbon steel. For pearlite in a 0.2 per cent carbon steel the readings are 490 to 1105, average 600. The different observers using the same Microcharacter found the following average values for the same sample of an 0.8 carbon steel: 600, 600 and 594. Cementite in white cast iron gave microhardness values of 4290 to 8600, an average of 5620. For tin the values varied from 10.7 to 16, an average of 12.2. For a sample of lead that had been processed to improve its purity the results varied from 4 to 6 with 5 as an average. Armco iron gave values of 177 to 490, average 240, while Swedish iron varied from 225 to 297, an average of 257. The results given in Tables 3 and 4 are taken from a series of 30 to 50 readings for each specimen.

TABLE 3

Observer	Sample Analysis	Microhardness α Phase			Cut Width, Microns, Eutectoid (Bronze)			Average Micro-hardness
		High	Low	Average	High	Low	Average	
1	Cu 70, Sn 10, Pb 20	225	135	167	3.50	3.1	3.20	960
2	Same	240	117	160				
1	Cu 70, Sn 2, Pb 28	167	77	102				
2	Same	167	83	107				
1	Cu 91.8, Sn 8.2	269	112	150	3.6	2.8	3.2	1,017
2	Same				3.4	2.8	3.1	1,014

For the cast bronze containing 8.2 per cent tin (Table 3), separate readings were recorded from the etched surfaces of the α structure for light grains and dark grains. For the light the values varied from 107 to 196, an average of 142, while the values were 210 to 232, an average of 217, for the darker grains. The material was in the unannealed cast condition, where considerable dendritic segregation was present.

TABLE 4

Observer	Width of Cut, Microns, for the α Phase in Cast Bronze											
	Specimen 1			Specimen 2			Specimen 3			Specimen 4		
	High	Low	Average	High	Low	Average	High	Low	Average	High	Low	Average
1	7.3	6.1	6.7	7.3	6.0	6.6	7.4	6.0	6.6	7.0	6.1	6.7
2	7.2	6.0	6.7	7.1	6.2	6.7	7.2	6.1	6.7	6.9	5.8	6.4
3	7.2	6.7	6.9	7.3	6.7	6.9						

In Table 4, No. 1 contained 24.5 per cent tin; No. 2, 20.3 per cent; No. 3, 24.5 per cent and No. 4, 27.3 per cent.

The samples used by observers 1 and 2 were annealed 50 hr. at 510° C. while those used by observer 3 were annealed 115 hr. at 510° C. The figures in Table 4 show that different observers using the same equipment can obtain results sufficiently close for all purposes.

S. R. Williams,* Amherst, Mass. (written discussion).—Mr. Swift has added another interesting study of hardness measurements by means of Bierbaum's standard hardness tester. I should like to present a few observations on the measurement of the width of the trace made by the diamond indenter of Bierbaum's instrument.

Can a standard criterion be set up concerning the location of the edge of the cut made by the Microcharacter? In Fig. 1 Mr. Swift shows what we would like to measure and also the measurement with which we have to be contented. This is the distance between the outer edges of the burr pushed up on both sides of the trace

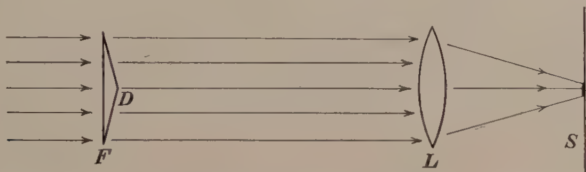

Fig. 12.—Arrangement of Fresnel biprism, lens and screen for measuring focal length of lens.

by the diamond. The criterion to be discussed here rests upon a procedure used for a number of years in the physics laboratory at Amherst in finding the focal length of a lens. If a Fresnel biprism is illuminated by sunlight (parallel rays of light), the dividing line between the two surfaces of the prism, obliquely inclined to each other, forms an excellent object, whose image is focused on a screen in finding the focal length of the lens, or of a concave mirror. Fig. 12 shows the arrangement of biprism, lens and screen. As the lens L is moved back and forth between the illuminated biprism F and the screen S, a distance that must be greater than four times the focal length of the lens, there comes a point where the image of the dividing line D of the prism comes into view on the screen. If the lens is moved toward the screen the line appears as a light line, but if the lens is moved toward the biprism the line appears dark. Only a slight movement of the lens causes the image of the line to snap from a dark to a light line, or vice versa. Just at that point, where the shade of the line suddenly changes, is the position for the proper focus of the line D. In this way the lens can be set accurately for a sharp image on the screen with a high degree of precision. Results may be repeated with surprising fidelity in observing the focal length of the lens.

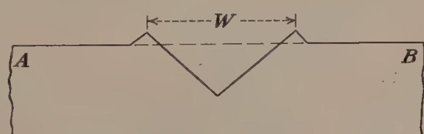

Fig. 13.—Width of cut as measured by biprism method is represented by W. This is smaller than B in Fig. 1.

In observing the cut made by the diamond of the Microcharacter, it will be found that a burr has been thrown up on each side of the cut in the form of a minute biprism. This burr acts optically, so the biprism does, in measuring the focal length of the lens. In focusing the microscope on such a cut one can see the top line of the burr snap suddenly from light to dark, which forms an ideal criterion for determining when the dividing line (top edge) of the burr is in focus. Fig. 13 shows that width is measured in this procedure. It is still not what we would like to have but it is nearer that desired position than the outside edges of the burr and we have a precise method of knowing when we have that position.

This effect is observable both for transmitted and for reflected light on the surface tested. My own impression is that it is better for transmitted light, but inasmuch as a

* Department of Physics, Amherst College.

great deal of my use of the Microcharacter has been with transparent plastics I may be biased in favor of illuminating the diamond cut by transmitted light.

A. J. Dornblatt,* Washington, D. C. (written discussion).—A test method as sensitive as the Bierbaum Microcharacter method for determining scratch hardness must be used with due regard to its sensitivity. A. M. Setapen* has observed that this test fails to differentiate between the hardness of annealed and cold-rolled silver when the scratch is made on polished silver surfaces. This apparently is due to the superficial layer of metal subjected to test, which, in the case of the special purity silver (99.995 per cent) in question, had been work-hardened by the metallographic polishing technique practically as much as could be produced by extensive cold-working.

Using the 9-gram load, and a micrometer microscope to measure scratch width, the following typical data were obtained:

Material	Scratch Width (at 500 ×), In.	
	Unpolished	Polished
Fully annealed silver	0.068	0.055
Cold-rolled silver, 25 per cent reduction	0.056	0.055

The same specimens tested on the unpolished surfaces as rolled were simultaneously mounted in Bakelite, and the mounting polished metallographically to a plane surface using relatively light polishing pressure.

Caution should be exercised in using the Bierbaum method when testing polished metal surfaces to determine the hardness of the metal or microconstituents below the polishing film.

C. F. Smart,† Pontiac, Mich. (written discussion).—The author mentions the frequently quoted theory that bearing metals should consist of both hard and soft components, usually of hard particles embedded in a soft matrix. The data given show that the cadmium-silver-copper alloys do not conform to this theory. These alloys have amply demonstrated, however, that they make excellent high-duty bearings and, further, some of the pure metals—lead, tin, cadmium and silver—function reasonably well as bearing materials over the ranges of load and temperature compatible with their strengths and melting points. Such facts would indicate that the duplex structure theory should be abandoned.

The data presented by the author lend additional weight to the belief that the fatigue life of a bearing metal is a function of the strength of the weakest component that is present to any appreciable degree in continuous phase. Accordingly, it is believed desirable, for example in tin-base babbitt, to maintain the antimony content at the upper limit of solubility of antimony in tin to obtain the matrix of greatest possible strength.

F. E. Carter,‡ Newark, N. J.—Has the Microcharacter been used for testing the hardness of electroplates? If so, on what metals and with what success?

C. H. Bierbaum.—The Microcharacter has been used very successfully in testing a large variety of commercial electroplates; among them chrome plate less than one-half one-thousandth of an inch thickness.

* Research Associate, American Silver Producers' Research Project.
† Metallurgist, Pontiac Motor Division, General Motors Corporation.
‡ Physical Metallurgist, Baker Platinum Works.

L. L. Swift (written discussion).—The comments of Mr. Bierbaum and Professor Conley are especially valuable, since they shatter an apparently erroneous belief regarding the Microcharacter. They have presented convincing evidence that different observers can check each other's readings.

In bringing up this point and others, it is hoped that those who use the Microcharacter in the future will have more concrete data to guide them in obtaining good results. Mr. Dornblatt's comment, for instance, stresses the fact that misleading values may be obtained if the specimen is not etched before being scratched.

Professor Williams' suggestion regarding a new criterion for the measurement of scratch width is certainly worthy of consideration. It would undoubtedly be convenient in measuring a microcut made in a transparent material, and could also be used for homogeneous metallic crystals. However, it is doubtful whether it could be used in measuring the scratch width of a heterogeneous material like the matrix of lead-base babbitt.

Professor Conley was evidently misled by a slight ambiguity in the text of the preprint. The figure "636" (p. 332, second paragraph) refers to the microhardness the writer obtained for the copper-tin crystals in tin-base babbitt (Table 1).

Special Methods for Polishing Metal Specimens for Metallographic Examination

By D. Beregekoff* and W. D. Forgeng*

(Detroit Meeting, October, 1938)

In the routine examination of a wide variety of metal specimens it is sometimes necessary to have special methods of polishing in order to retain and reveal certain details in each specimen. Among such special cases is the retention of graphite in malleable and gray cast irons, the preservation of all types of nonmetallic inclusions in both hard and soft steels, obtaining a scratch-free surface with soft metals, and avoiding the usual relief effects with very hard specimens such as tool metals containing various carbide and nitride phases. It is the purpose of this paper to give an account of some of these special polishing methods in use at the Union Carbide and Carbon Research Laboratories.

The polishing procedures outlined have been found to give uniform results. It is obvious that only general rules and the most important working details can be given here. Following these rules, the polisher can obtain satisfactory results if he possesses the necessary patience and has a sincere desire to give as nearly perfect a finish as possible to his work.

Procedure

The specimen is flattened with considerable care on a file or sharp cutting sanding belt, since the initial production of a flat surface greatly facilitates subsequent polishing. The polishing motors have two speeds, 600 and 1200 r.p.m. At higher speeds specimens are likely to be overheated, therefore the high speed is used only when a saving of time is important.

The following abrasive papers are used consecutively: No. 2, No. 1, No. 0, No. 00 and No. 000. The final wet polishing is done on a cloth-covered metal disk. Woolen broadcloth of the best quality and capable of resisting severe pressure is most commonly used on the last lap. A polishing felt of the type used for polishing optical glass has been found equally satisfactory and is much stronger than broadcloth. For retaining inclusions and graphite, a hard cloth with very little resilience, such as

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* Union Carbide and Carbon Research Laboratories, Niagara Falls, N. Y.

airplane fabric (Flightex-Fabric) or an unbleached muslin, is employed. A soft silk velvet is used as a final cloth after completion of polishing on other cloths in order to remove all scratches.

Either relevigated alumina or magnesia* is used as the abrasive on the cloth laps. The best surfaces are obtained when the time of polishing on cloth laps is kept at a minimum. After the No. 000 paper has been used, the scratches are still too deep to be removed rapidly on the cloth, so that the specimen is finished on worn No. 000 paper that has been coated with graphite applied by rubbing the paper with a piece of graphite electrode.

The polishing on cloth, except of cast-iron specimens, must be performed with a circular motion. If it is done in one direction comet-like tails appear at the inclusions. The cloth is kept moist and is washed with soap and water as soon as it becomes dirty and gritty. The specimen is pressed firmly against the cloth until the scratches from the graphite-coated paper are removed, then the pressure is gradually reduced. Very fine scratches are left on the specimen by this treatment. When it is necessary to remove them, a silk velvet lap charged with the finest relevigated alumina is used. For more specific details of the polishing process and of the precautions to be taken during polishing, the reader is referred to earlier papers from these Laboratories.[1–4]

Most specimens are polished in the manner described above. In special cases, however, certain departures from this procedure are required. These will be considered individually.

Graphite in Cast Iron

Graphite sometimes remains intact in gray or malleable iron even if the specimens are polished in the usual way. More frequently, however, graphite is pulled out by particles of the abrasive paper and dislodged by broadcloth. Experience has shown that in order to eliminate this it is necessary to polish the specimens for a much longer time, especially on the No. 2 paper. Well-worn No. 2 paper is preferable to new.

When properly prepared, no black spots (indicative of dislodged graphite) are seen at 100 diameters after polishing on graphite-coated No. 000 paper. The scratches of this last paper are removed on airplane wing-covering material, using "heavy" magnesia as the abrasive. The cloth is damp but not wet, and firm pressure is applied. The microscope is employed frequently to determine when the graphite is revealed satisfactorily, so that the polishing will not be carried too far. Graphite is frequently washed out by rotation, so the specimen is polished in only one direction on the cloth. The "comet tails" formed at first disappear with further polishing.

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* Heavy magnesia is used for some specimens and light magnesia for others.

[1] References are at the end of the paper.

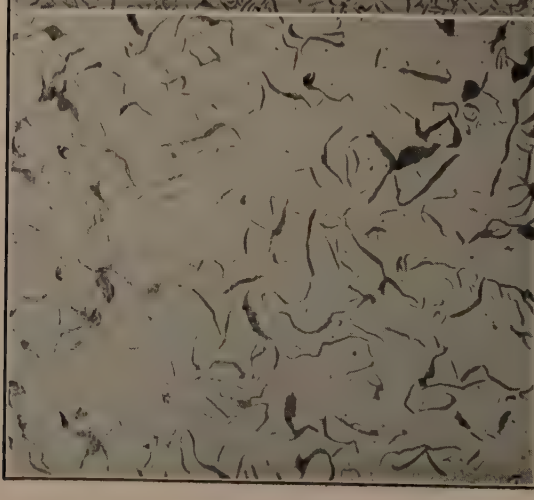

FIG. 1.—COARSE GRAPHITE FLAKES IN GRAY CAST IRON. × 100.

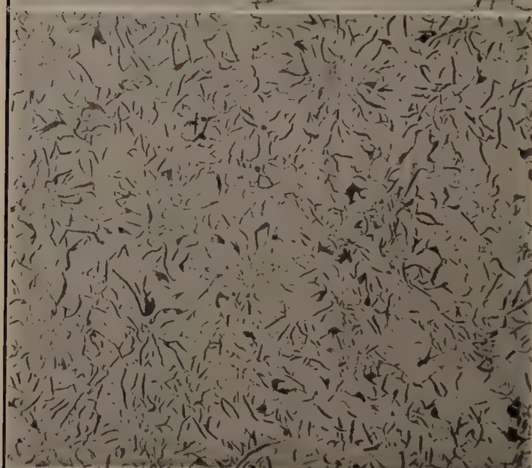

FIG. 2.—FINE GRAPHITE FLAKES IN GRAY CAST IRON. × 100.

FIG. 3.—GRAPHITE NODULES IN MALLEABLE CAST IRON. × 100.

This procedure for polishing cast iron is somewhat slow. The time on cloth for a specimen of gray iron ½ in. square is 10 to 20 min., and for a specimen of malleable cast iron of the same size it is 40 to 50 min. The time varies with the hardness of the metal.

Examples of properly polished cast irons are shown in Figs. 1 to 3 inclusive.

Preserving Inclusions

Specimens in which the inclusions must be retained are polished in the usual way to the No. 000 graphite-coated paper. Here, however, polishing is continued until the scratches are almost invisible to the naked eye. This exposes the inclusions and simplifies the subsequent polishing on cloth. Broadcloth washes out many kinds of inclusions. To preserve them intact, airplane wing-covering material is used with fine alumina or "light" magnesia as the abrasive. Scratches left after polishing on this cloth are often removed without dislodging the inclusions by finishing on velvet with the finest relevigated alumina.

Specimens having easily removable inclusions, such as alumina, are polished on airplane wing covering with "light" magnesia as the abrasive. During polishing the cloth is not too wet and is almost dry at the finish. Velvet cannot be used to remove scratches on these specimens because it tears out this type of inclusion.

Photomicrographs of typical inclusions in steel are shown in Figs. 4 and 5. Fig. 6 is a photomicrograph of a leaded bronze in which the soft lead constituent was retained by the same procedure that is used for preserving inclusions in steel.

Soft Metals

Specimens of moderately soft metals are cut very carefully to avoid any deep distortion of the surface to be polished. The sample is then flattened by means of very light pressure across a file. In order to remove disturbed metal, polishing on subsequent papers is prolonged more than usual. The scratches from the last paper are removed by polishing on broadcloth with fine alumina. The final polishing on cloth is first in the direction of the scratches of the last paper and later with a circular motion. If a circular motion is used at first the scratches are filled with flowed metal and only seem to be removed; they reappear after etching. Any scratches remaining on the specimen after polishing on broadcloth are removed by polishing on velvet with the finest alumina and soap. Unless the velvet is saturated with soap and abrasive it smears the soft metals very badly.

With very soft metals such as pure lead, tin or aluminum, the emery particles of the abrasive papers are often embedded during polishing and

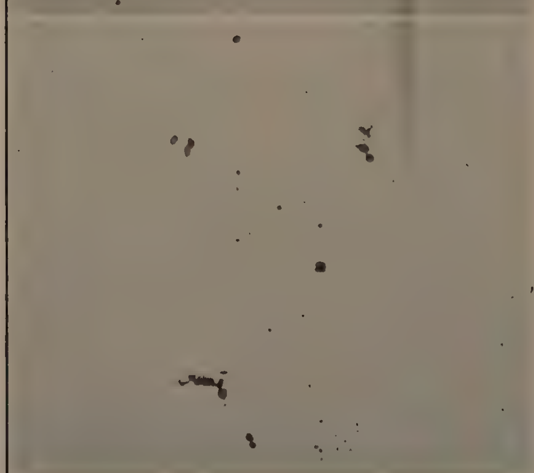

Fig. 4.—Alumina inclusions in steel. × 100.

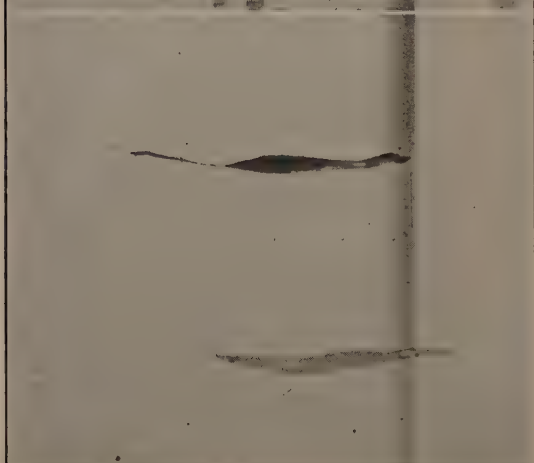

Fig. 5.—Sulphide (light) and silicate inclusions in steel. × 500.

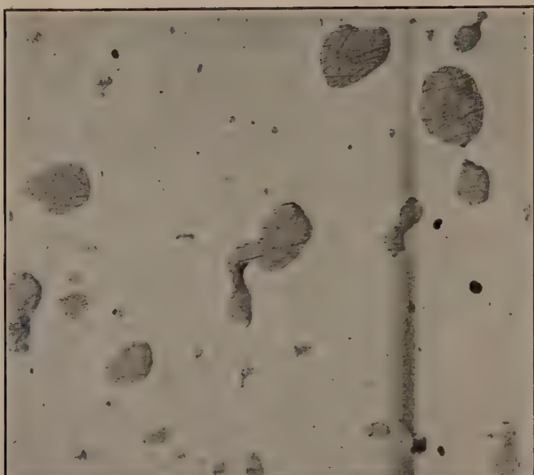

Fig. 6.—Leaded bronze. × 250.

it is very difficult to remove them. Therefore these metals, after smoothing on a clean fine file, are taken directly to a broadcloth lap. The cloth is charged with the finest alumina and abundantly supplied with soap and water. At the start, some pressure is used but when all traces of the file are removed the pressure is lightened considerably. In this way a surface bright and clean enough for etching purposes is obtained.

If new cloth, such as glass-polishing felt, is used it is possible to remove scratches and polish lead without abrasives, using only copious quantities of water and soap. Sharp structural definition is obtained

FIG. 7.—PURE LEAD, ETCHED. × 100.

when the specimen is suitably etched. This is illustrated in Fig. 7, which shows a specimen of lead that was polished in this manner and etched by the following procedure: The etching solution consisted of a mixture of 2 to 3 parts of glacial acetic acid and 1 part of hydrogen peroxide. The etching time was 4 to 5 min. The specimen was shaken as vigorously as possible without interruption during the etching. On being taken from the solution, the specimen was immediately washed with hot water and with alcohol without exposure to air. In this way the grains are revealed very clearly. If the specimen is permitted to remain over the vapors of the solution, even for a short time, the grains are colored various hues.

HARD METALS

The very hard metals, such as Stellite tools and tungsten carbide alloys, are polished on special diamond-impregnated polishing disks. These disks are furnished in coarse and fine grit sizes. A flat surface suitable for ordinary examination is obtained in a few minutes with these

abrasive wheels. The scratches left by the finer diamonds may be removed without excessive relief effects in a short time on a broadcloth lap saturated with alumina.

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DISCUSSION

(*Ernest B. Drake presiding*)

W. L. Meinhart,* Chicago, Ill. (written discussion).—The art of metallographic polishing is so broad, and has so many peculiarities, depending on the nature and type of alloy dealt with, that in the present discussion no attempt will be made to cover the entire field. Our remarks will thus be restricted primarily to the polishing of malleable and gray iron, which present the difficult problem of retaining graphitic inclusions intact.

The procedure that gives us the best result is very similar to that described by the authors through the fine emery paper stage. However, instead of rubbing graphite on worn No. 000 paper, as the authors do, we apply paraffin dissolved in benzol and rub it smooth with a piece of cotton. For the first wet lap, a worn, stiff-nap velvet cloth is used, into which a little of the paraffin-benzol solution has been worked, until the surface is smooth. A thin, soapy paste of 600-mesh alundum is used as abrasive, and the speed of the polishing wheel is adjusted to 350 r.p.m. In the final polishing stage, we use a velvet-cloth wheel, coated with a thin paste of No. 1 levigated alumina. Water is applied in amounts just sufficient to make the paste slippery, and the polishing speed is adjusted to 550 r.p.m. According to our observations, medium stiff-nap velvet holds the abrasive better than silk or satin cloth, and if used as suggested, does not result in "dragging" out of the graphite.

It is our experience that polishing of malleable iron samples frequently causes the metal to flow and "smear" over the edges of graphitic nuclei, thus erroneously reducing them in size. Fig. 8, which is very similar to the author's Fig. 3, is an example of such an occurrence. To remedy it, as we have found out, alternate polishing and etching is necessary, starting with the 600-alundum stage. It seems that the etching reagent attacks and loosens the flowable metal film covering the edges of the graphite, while the subsequent polishing removes it.

The results obtained by our method of polishing are illustrated in Fig. 9, which has been produced in the same sample as illustrated in Fig. 8, and which in our opinion is the correct appearance of graphite noduli. Notice the sharp outlines of the graphite and sulphide inclusions.

We have found out that etching four or five times in 5 per cent Nital is sometimes necessary to clearly define the graphite. Care must be taken not to overetch annealed malleable iron, because wide grain boundaries, which are difficult to remove in the final polishing, may develop.

Figs. 10 and 11 are illustrations of the same structure as shown in Fig. 9, but taken at lower magnifications.

Careful examination of Fig. 10 reveals the aforementioned "wide grain boundaries," which are an indication of the first stage of overetching.

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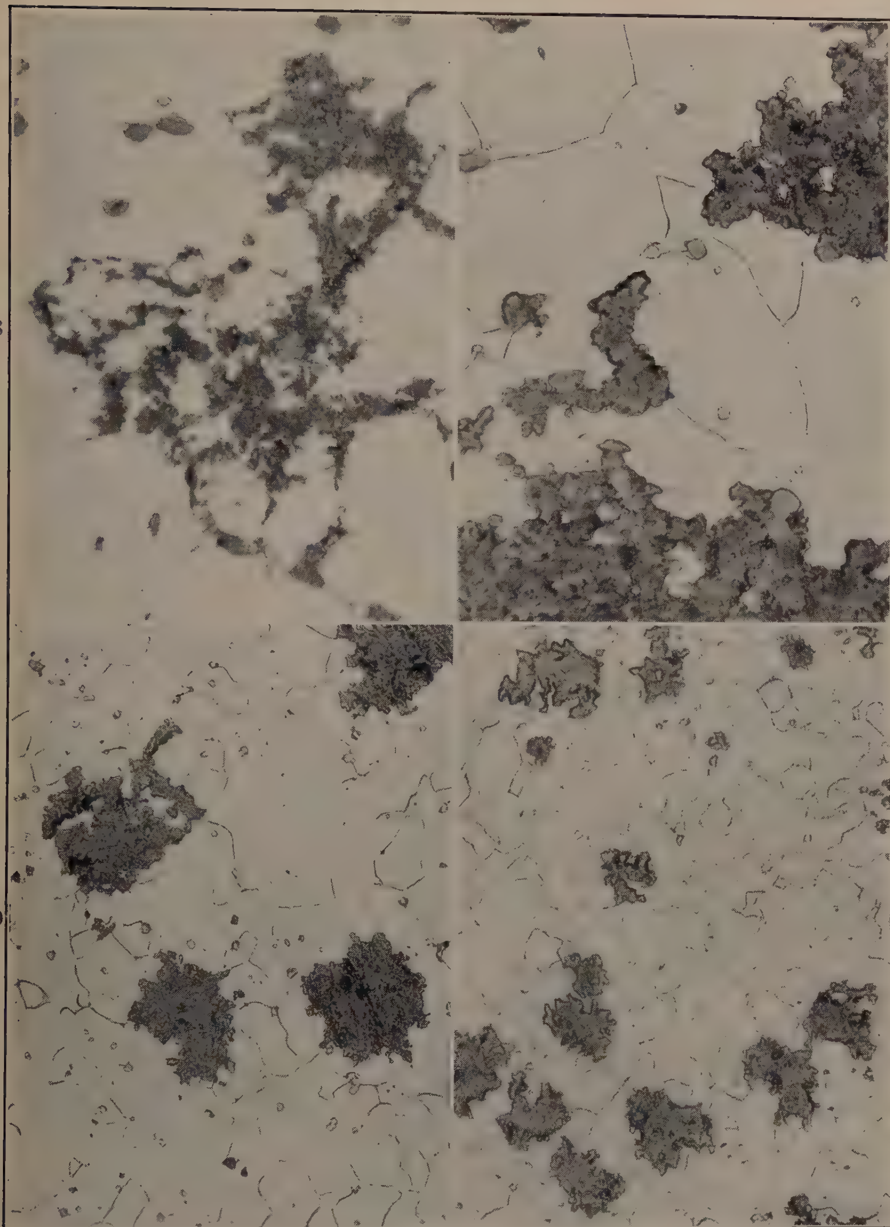
* Crane Company.

8 9



10 11

FIG. 8.—FULLY ANNEALED MALLEABLE IRON PREPARED WITHOUT ALTERNATE ETCHING AND POLISHING. × 500.

FIG. 9.—SAME AN FIG. 8, PREPARED BY ALTERNATE ETCHING AND POLISHING METHOD. × 500. FINAL ETCH, 5 PER CENT NITAL.

FIG. 10.—FULLY ANNEALED MALLEABLE IRON, SAME AS FIG. 9. × 150. FINAL ETCH, 5 PER CENT NITAL.

FIG. 11.—SAME AS FIG. 10. × 100. FINAL ETCH, 5 PER CENT NITAL.

The average time period necessary to obtain the aforedescribed results on malleable iron is about 75 minutes.

Figs. 12 and 13 are illustrations of a gray iron and of a free-machining, high-sulphur steel, respectively, also polished according to the method just described.

In the taking of all these photomicrographs, panatomic film was used because of its low contrast. The more contrasty film darkens the graphite and obscures its inner structure.

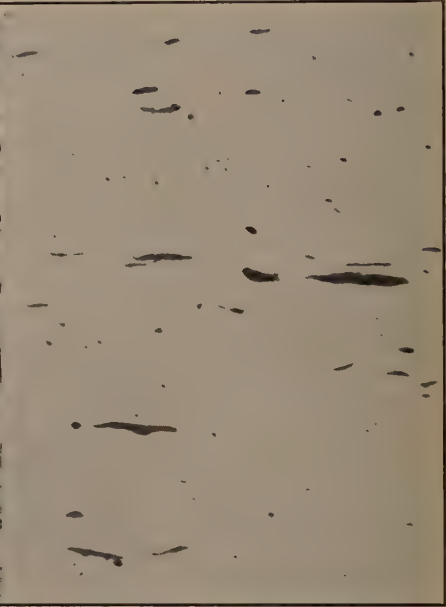


Fig. 12. Fig. 13.

Fig. 12.—Gray cast iron prepared by alternate etching and polishing method. × 150. Final etch, 5 per cent Nital and Picral.

Fig. 13.—Free-machining steel showing manganese sulphide inclusions polished by above method. No final etch. × 500.

G. Edmunds,* Palmerton, Pa.—Have the authors been able to reduce the relief in metallographically polished specimens having small, hard constituents in soft matrices?

W. D. Forgeng and D. N. Beregekoff (written discussion).—In answer to Mr. Edmunds' question, we can only state that, in general, relief may be reduced in metallographic specimens having hard constituents in soft matrices if the time of polishing on cloth is kept at a minimum. This requires that specimens be very carefully and lightly polished on the graphite-coated No. 000 paper before proceeding to the cloth-covered laps.

The results obtained by Mr. Meinhart are excellent and require little comment. It is our opinion, however, that the true structure of the graphite nodules is revealed in Mr. Meinhart's Fig. 8 and our Fig. 3. We believe that the roughened appearance of the nodules in Figs. 9, 10, and 11 is the result of removal of a ferritic constituent from the nodules by the etching reagent.

* Research Division, New Jersey Zinc Co.

INDEX

(NOTE: In this index the names of authors of papers and discussions and of men referred to are printed in SMALL CAPITALS, and the title of papers in *italics*.)

CONTENTS OF VOLUME 135*

Transactions A.I.M.E., 1939

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